U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-298 841

Proceedings of the Workshop on Alternatives for Cadmium Electroplating in Metal Finishing, Held at National Bureau of Standards, Gaithersburg, Maryland on October 4-6, 1977

(U.S.) Environmental Protection Agency, Washington, DC

Prepared for

Consumer Product Safety Commission, Washington, DC

Mar 79

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

EPA-560/2-79-003
March 1979

Toxic Substances

PB 298841

EPA

Proceedings of the Workshop On Alternatives For Cadmium Electroplating In Metal Finishing

October 4—6, 1977

Sponsored by:
Consumer Product Safety Commission
U.S. Department of Commerce
U.S. Department of Defense
U.S. Department of Health, Education, and Welfare
U.S. Department of the Interior
U.S. Department of Labor
Environmental Protection Agency
General Services Administration
at the
National Bureau of Standards
Gaithersburg, Maryland

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-560/2-79-003

2.

3. RECIPIENT'S ACCESSION NO.
PB298841

4. TITLE AND SUBTITLE
PROCEEDINGS OF THE WORKSHOP ON ALTERNATIVES FOR CADMIUM ELECTROPLATING IN METAL FINISHINGS; October 4-6, 1977

5. REPORT DATE
March 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Dage, E., Dyckman, E., Isler, W. and Ogburn, F. (editors)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Office of Toxic Substances (TS-792)
Environmental Protection Agency
Washington, D.C. 20460

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency; Consumer Product Safety Commission; Dept. of Commerce; Dept. of Defense; Dept. of Health, Education and Welfare; Dept. of the Interior; Dept. of Labor; General Services Administration

13. TYPE OF REPORT AND PERIOD COVERED
Workshop Proceedings

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This publication compiles the proceedings of the Workshop on Alternatives for Cadmium Electroplating in Metal Finishing held October 4-6, 1977 which was jointly sponsored by seven Federal agencies. The workshop was prompted by the concerns of government agencies for the potential environmental damage resulting from current cadmium eletroplating pratices and the high rate of government use of electrodeposited cadmium. The workshop examined techniques and alternatives to minimize the environmental losses of cadmium from electroplating by (a) applying cadmium by mechanisms that reduce the loss of cadmium during plating and (b) developing suitable and cost-effective alternative materials, methods, and coatings. The workshop included presentations on the Federal and industrial concerns for the commercial significance, environmental effects, and health effects of cadmium. Panel discussions reviewed the topics "Are specifications and standards barriers to change " and "How essential is electrodeposited cadmium?".

These proceedings were compiled from statements submitted by the participants for publication and from edited transcripts of discussion periods.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
metal finishing electroplating cadmium zinc tin aluminum water pollution waste treatment corrosion manganese phosphate fasteners		

18. DISTRIBUTION STATEMENT
Document is Available to public through
National Technical Information Services
Springfield, VA 22151

19. SECURITY CLASS (This Report)
Unclassified

20. SECURITY CLASS (This page)
Unclassified

21. NO. OF PAGES
634

* U.S.G.P.O. 620-007/1302-3782

EPA-560/2-79-003

PROCEEDINGS OF THE
WORKSHOP ON ALTERNATIVES FOR CADMIUM ELECTROPLATING IN METAL FINISHING,

October 4-6, 1977

Sponsored by:

Consumer Product Safety Commission
U.S. Department of Commerce
U.S. Department of Defense
U.S. Department of Health, Education, and Welfare
U.S. Department of the Interior
U.S. Department of Labor
Environmental Protection Agency
General Services Administration

at the

National Bureau of Standards
Gaithersburg, Maryland

Elbert Dage
Edward Dyckman
William Isler
Fielding Ogburn

Editors

March 1979

DISCLAIMER NOTICE

Convention of this Workshop on Alternatives for Cadmium Electroplating in Metal Finishing and publication of this document do not signify that the contents necessarily reflect the joint or separate views and policies of each sponsoring Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENT

This document was reproduced by the Environmental Protection Agency. Transcription services for the Workshop were provided by the Occupational Safety and Health Administration. Transcripts of the dialogue taking place during the workshop were edited by Fielding Ogburn, National Bureau of Standards; William Isler, Harry Diamond Laboratories; Elbert Dage, Environmental Protection Agency; and Edward Dyckman, Defense Industrial Resources Support Office.

Additional Copies Of This Report May Be Ordered From The

National Technical Information Service
U.S. Department of Commerce
5185 Port Royal Road
Springfield, Virginia 22151

FOREWARD

Forty two representatives of government and one hundred eighteen representatives of industry participated in this Government organized workshop, "Alternatives for Cadmium Electroplating in Metal Finishing" held 4-6 October 1977 at the National Bureau of Standards, Gaithersburg, Maryland.

The workshop was sponsored and organized by a steering committee composed of representatives from the Consumer Products Safety Commission, Department of Commerce, Department of Defense, Department of Health, Education and Welfare, Department of the Interior, Department of Labor, Environmental Protection Agency, and the General Services Administration.

The workshop was prompted by the concern of government agencies over environmental damage resulting from present day cadmium electroplating processes. Cadmium electroplating and stripping operations are responsible for as much as fifty percent of the industrial discharges of cadmium to water in the United States. Cadmium that reaches drinking water supplies, navigable waters, and food chains is hazardous to humans.

The purpose of the workshop was to examine techniques and alternatives to minimize the loss of cadmium into the environment by (a) applying cadmium by mechanisms that reduce the loss of cadmium during plating and (b) developing suitable and cost-effective alternative materials, methods, and coatings that can be utilized where possible in the design and manufacture of items that are now characteristically electroplated with cadmium.

A secondary purpose of the workshop was to develop a model of a technical forum in which government and industry representatives could discuss a wide spectrum of issues concerning the use of and alternatives for industrial materials suspected of being hazardous to health and the environment. Similar workshops concerning other materials might be organized in the future by agencies responsible for regulating the use of toxic substances.

The concept adopted by the steering committee was to divide the workshop into two sessions. The first session concentrated on presentations reporting the efficacy of individual alternative materials and processes for electrodeposited cadmium. The second session dealt with the presentation of laboratory and field trials comparing a number of the alternatives described during the first session. Interspersed throughout these presentations were a number of papers on closely related areas, including the development of environmentally compatible processes for electroplating cadmium, the importance of electrodeposited cadmium coatings, and the environmental and health effects of cadmium.

In addition to presentations, two panel sessions were held. The first panel addressed the question, "Are specifications and standards barriers to change?" Panelists were individuals with current responsibilities or backgrounds in the preparation and use of government and industry specifications and standards. They extemporaneously discussed problems and issues related to the identification, testing, qualification, documentation, and application of alternative materials and processes for electrodeposited cadmium. The second panel addressed the question, "How essential is electrodeposited cadmium?" Panelists included platers, cadmium suppliers and cadmium users. They discussed technical, economic, environmental, and health issues germane to the production and use of electrodeposited cadmium.

This document presents the proceedings of the workshop, including an edited transcript of the dialogue from question and answer periods following each presentation and from each discussion panel. The workshop proceedings will be used by participating agencies in their efforts to assess the various approaches to minimizing loss of cadmium to the environment.

The information presented during this workshop is of timely importance, not only to the government, but to the industrial community as well. To avoid delays in the dissemination of this information, this report has been produced directly from statements submitted by the participants for publication.

CONTENTS

WORKSHOP ON ALTERNATIVES FOR CADMIUM ELECTROPLATING IN METAL FINISHING

National Bureau of Standards
Gaithersburg, Maryland

October 4-6, 1977

PAPERS PAGE

Introductory Remarks 1

Emanuel Horowitz, Deputy Director, Institute for Materials Research, National Bureau of Standards

Introductory Remarks 5

George Marienthal, Deputy Assistant Secretary of Defense for Energy, Environment and Safety

A New Strategy for Controlling Priority Water Pollutants 9

Ernst Hall and Dev Barnes*, Effluent Guidelines Division, Office of Water Planning and Standards, Environmental Protection Agency

Cost Effectiveness for Cadmium Waste Treatment in the Electroplating Industry 15

Kenneth J. Yost, Institute for Environmental Health, Purdue University

---

* Presented Paper

PAPERS PAGE

Surface Alloying by Ion Implantation: An Alternative to Cadmium Electroplating 41

B. D. Sartwell and F. X. McCawley, College Park Metallurgy Research Center, U.S. Bureau of Mines

Ion Vapor Deposited Aluminum Coatings 67

E. R. Fannin, McDonnell Aircraft Company

Cadmium in Food and Drinking Water - FDA Considerations 87

George L. Braude and Samuel Shibko, Public Health Service, Food and Drug Administration

Cadmium Plating with Environmental Restrictions 103

L.E. Vaaler and J. Gurklis, Battelle-Columbus Laboratories

Outstanding Corrosion Protection Provided with Zinc Flake in a Water-Based Coating 113

J. A. deRidder and J. R. Kovelan, Diamond Shamrock Corporation

A Practical Wet Impact Alternative to Cadmium Electroplating 135

Lester Coch, Waldes Kohinoor, Inc.

Electrodeposition of Zinc-Nickel Alloy Coatings 171

J. W. Dini and H. R. Johnson, Sandia Laboratories
(Presented by Donald J. Levy, Lockheed Research Laboratory)

Corrosion Resistant Coatings Containing Lubricating Solids As an Alternative to Cadmium Electroplating on Fasteners & other Hardware 207

G. R. Kliemann and D. J. Sargent, E/M Lubricants, Inc.

Artificial Shellfish for Monitoring Ambient Cadmium Levels in Seawater 215

William B. Kerfoot, Environmental Devices Corporation

Unique Characteristics of Cadmium Electroplating 241

Albert R. Cook, International Lead Zinc Research Organization, Inc.

The Properties of Cadmium and Tin-Zinc Electrodeposits 259

John M. Bihl, Tin Research Institute

PAPERS PAGE

The Advantages of Chloride Zinc Plating 289

Edward R. Jorczyk, 3M Company

Manganese Pressure Phosphate Coatings as a Substitute for Cadmium Coatings 307

Henry Crain, Rock Island Arsenal, Department of the Army

Effects of Cadmium in the Environment 325

Calvin Menzie, U.S. Fish and Wildlife Service

A New Non-Cyanide Cadmium Electroplating Bath 365

Edward R.Jorczyk, 3M Company

Bonded Solid Dry Film Lubricants as an Alternative to Cadmium Electroplating 381

Theodore M. Pochily, Watervleit Arsenal, Department of the Army

Alternatives for Cadmium Metal Deposition in the Field of Mechanical Plating 409

Edward A. Davis, 3M Company

State of the Art for High Rate Sputter Deposition 423

E. D. McClanahan, R. W. Moss, N. Laegreid, J. W. Patten, R. A. Busch, M. A. Bayne, and E. N. Greenwell

Cadmium as a Commodity 465

John M. Lucas and John M. Hague, U. S. Bureau of Mines

Replacement of Cadmium Electroplating on IBM Hardware 479

Allen W. Grobin, Jr., IBM Corporation

Evaluation of Coated Fasteners: Alternatives To Cadmium Plating 495

H. J. Dolejs and R. E. Geisert, Gould, Inc.

Evaluation of Protective Coatings for Army Ordnance Items 519

A. Edwards and W. E. Isler, Harry Diamond Laboratories, Department of the Army

PAPERS PAGE

Corrosion Performance of New Fastener Coatings on Operational Military Aircraft 541

Fred H. Meyer, Jr., Air Force Materials Laboratory and Edward Jankowsky, Naval Air Development Center

The Ideal Aerospace Fastener Coating 555

E. Taylor and J. Laurilliard, Standard Pressed Steel Company

Appendix I - 571

Panel Discussion: "Are Specifications and Standards Barriers to Change?"

Appendix II - 585

Panel Discussion: "How Essential is Electrodeposited Cadmium?"

Appendix III - 607

Attendance List

Appendix IV - 617

Sponsoring Agencies and Representatives

Appendix V - 621

Aerospace Industries Association Surveys on Alternatives to Cadmium Plating

Appendix VI - 637

Results of Workshop Questionnaires

INTRODUCTORY REMARKS

DR. EMANUEL HOROWITZ, DEPUTY DIRECTOR
INSTITUTE FOR MATERIALS RESEARCH
NATIONAL BUREAU OF STANDARDS

I want to welcome you to the National Bureau of Standards on behalf of the Institute for Materials Research.

Some of you may be visiting the Bureau for the first time, and may not be very familiar with what we do here. I thought it would be worthwhile to take a few minutes to tell you something about the Bureau.

The Bureau was established in 1901 and it was meant to function as the National Measurement Laboratory with responsibilities for developing national standards, improved and new methods of measurement in the field in engineering and science, and to provide a focal point in the United States Government for standardization activities.

In 1965 the Bureau of Standards was reorganized into its current structure. It consists of four major organizational units, or institutes. The largest one is the Institute for Basic Standards which provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with the measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce.

There is also an Institute for Applied Technology which provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government; cooperates with public and private organizations leading to the development of technological standards (including safety standards) and codes and methods of test; provides technical advice and services to government agencies upon request; monitors NBS engineering standards activities, and provides liaison between NBS and national and international engineering standards bodies; and carries out programs falling into three broad categories: (1) those which are safety related, (2) those which relate to improving the industrial economy and to facilitating domestic and international commerce, and (3) those which relate to improving the efficiency of governmental operations.

The Institute for Computer Science and Technology has the responsibility for the standardization of hardware and software in the computer field, particularly with respect to purchases by the Federal Government.

The Institute for Materials Research, which is a co-sponsor of this meeting, has as its mission the assistance and stimulation of industry in the development of new and improved products and the full utilization of existing products through increased understanding of basic properties of materials. The Institute (a) develops, produces, and distributes standard reference materials for the calibration of instruments and equipment, the comparison of measurements on materials, and for assistance in the control of production processes in industry and in laboratories that are of direct benefit to the general public, e.g., clinical laboratories and air pollution laboratories; (b) conducts research on the properties and performance of materials which are of importance to industry, commerce, science, and the general public, as well as the collection and dissemination of data on these properties; (c) develops techniques for the preparation of special research materials and for the measurement of their properties; (d) develops criteria and tests, including nondestructive tests, by which the performance characteristics of materials may be evaluated; (e) provides advisory and research services for other agencies; and (f) assists national and international standardization organizations in developing methods of measurement and establishing standards for materials.

In recent years, we in IMR have focussed on a number of national problems, one of which is the general problem that you are here to discuss this morning. I will touch on that briefly in a moment.

Some of our major programs at the present time concern the utilization and the conservation of materials in society. We have a major program in failure analysis (how and why do things fail) trying to predict the performance of materials so that materials can be properly used in design and then maintained properly.

We are concerned with clinical chemistry measurements, and measurement and standards matters related to health. For example, we have a major program in developing referee or definitive tests to make the clinical analyses that are performed by approximately 15,000 clinical laboratories in this country more accurate and meaningful. Last year there were about 5 billion clinical measurements made in the United States. We are also providing standard reference materials for calibrating instruments and measurement methods so that analytical results can be compared from one laboratory to another.

We are concerned with accurate measurements for air and water pollution. While we are not responsible for the regulatory aspects of the environment, we are concerned with providing accurate methodology and standards for the analysis of particulates, trace metals, organics, and some of the gases which are found in the environment. These methods, can then, be adapted by the Environmental Protection Agency for some of their monitoring activities and are available for industry use.

One of the problems that we have been concerned with over the last three years in this latter program has been the analysis of toxic metals in the environment. We have been particularly concerned with the chemistry of heavy metals in the Chesapeake Bay. We have published a number of papers describing the chemical transformations involving mercury and other heavy metals that occur in the sediment of Chesapeake Bay; specifically, those reactions involving strains of pseudomonas bacteria and traces of tin which result in the transformation of non-toxic inorganic mercury to methylated (organic) mercury.

That brings me to the question of other heavy metals, including cadmium which is under consideration at this workshop. We share your concern about heavy metals finding their way into the environment. It is an important health effects problem, and we need to understand the reaction mechanisms involving heavy metals which lead to toxic compounds. There is also a question of the conservation of cadmium as a strategic and critical material.

To conclude with a brief comment on electrodeposition efforts, NBS has been active in this field since 1913. As many of you may know, NBS scientists invented several forms of electrodeposition, including electroless nickel. The staff concerned with electrodeposition at NBS over the years has published more than 300 technical reports, including the mechanical properties and the corrosion characteristics of some of the electrodeposited materials. We have a strong interest in the subject that you are due to discuss here and we will be following the discussions with keen interest.

INTRODUCTORY REMARKS

MR. GEORGE MARIENTHAL, DEPUTY ASSISTANT SECRETARY OF DEFENSE FOR ENERGY, ENVIRONMENT, AND SAFETY

I appreciate the opportunity to be here with you this morning. I want to thank those of you from industry, from the academic world,and from Federal agencies for being here this morning and for your thoughtful papers. Without that support, this workshop would not be possible.

I represent the Department of Defense in the areas of energy, environment and safety. The Department of Defense is vitally concerned with each of those issues. In the energy area, we are working with the newly formed Department of Energy, which was created last Saturday. The Defense Department is a large consumer of our nation's energy and, as a result, we have petroleum logistics problems. We must, for example, ask the question of "where do we place our petroleum in order to make sure that our fleet and other mobile forces are run properly during times of emergency?" Our more mundane activities involve the operation of thousands of installations in an energy-conservation manner.

Hopefully, one issue during this conference will be the recognition that energy is a problem and, as we are looking at alternative processes and substitutes, the question of energy should be considered.

I also represent the Department in areas of occupational safety and health. We are a very large employer, employing about 3 million people. These employees deserve a healthful working place, and my responsibility is to try to provide that under such laws as the Occupational Safety and Health Act.

Without going into occupational safety and health further, suffice it to say that all employers today have a major problem in providing that safe work place.

You may have seen in the media today that the National Institute of Occupational Safety and Health has recently completed a major report. Dr. Finklea of NIOSH announced that they had surveyed a large population of employers, including a high percentage of those who employed more than 500 people, and had found that one out of every four employees was subjected to hazardous materials and other hazards which would be injurious to their health.

Our mutual concerns with safety and occupational health are among the reasons we are here today. This issue will relate to the output of this workshop.

I am concerned with and represent DoD in the area of environmental protection. We are,of course,doing the best we can in air pollution, water pollution, safe drinking water, radiation, solid waste management and the myriad of such laws that affect our day-to-day operations in the Department of Defense.

Preceding page blank

Paramount in this workshop is the question of environmental protection.

It is not unusual at all, therefore, for the Department of Defense to be a co-sponsor of this workshop. We became interested in cadmium more than two years ago, and this workshop is a direct result of our interest.

The bulk of the credit for bringing this about belongs to Mr. Ed Dyckman, who works for the Department of Defense.

In any event, the Department of Defense has addressed cadmium uses, alternative processes, and possible substitutes for several years. I would like to say that the Defense Department does not have any preconceived notions as to the future of cadmium.
There may be many of you here today who will say: "Cadmium is the greatest thing. It is absolutely essential, and all we have to do is improve plating processes from an environmental protection point of view."

There are others who are saying, "Cadmium is bad,and it must be banned." I suppose that there are a lot of you who have an opinion someplace between these two.

I am not standing up here taking any side,and I am hopefully exploring alternatives and all aspects of this issue. The DoD placed special interest on our cadmium uses in early 1975, primarily due to some outside pressure from an environmental group. The environmental group became concerned with heavy metals from the Philadelphia sludge that was being ocean-dumped, which you still can read about today. The Philadelphia EPA office in Region III has recently extended the permit for ocean dumping.

The environmental group knew that there was a high concentration of heavy metals in the sludge and selected cadmium as an example. They started asking questions such as "How did cadmium get there to begin with?" In response, the electroplaters of the area indicated that Department of Defense contracts caused the cadmium to be in the sludge, and the Department of Defense is predominantly the number one user of cadmium and,therefore, it is their fault. This brought me into the problem in a hurry.

This pressure was most helpful. It caused us to study cadmium comprehensively, and it caused us to look at our use of it in the Department of Defense, specification by specification.

The truth is that we consume, or cause industry to consume, about 5.2 percent of the U.S. annual consumption of cadmium. The bulk of cadmium is used, as you know, in electroplating, and of that, the DoD is responsible for consuming less than seven percent of the total. Therefore, we do not wish to continue to carry the total burden on us from the environmental groups.

That is why we are thankful for you being here today, to help us carry that burden.

As we began to study our usage of cadmium from several points of view, the primary concern was to protect public health and welfare, as dictated by the laws concerning safety, occupational health, and environmental protection, such as the Federal Water Pollution Control Act, Section 307 and Section 304-B, and the Toxic Substances Control Act.

Our second concern was to develop a sound working relationship with the U.S. Environmental Protection Agency in the area of cadmium.

We carried out that cooperative effort over the past two and a half years, and this workshop is evidence that it is going well.

Thirdly, we are always interested in improving our materials processes and, therefore, we initiated our own study to identify alternatives for cadmium. Our study did identify options and many of those are, of course, described in your papers. *

We are very interested in continuing our cooperative efforts with industry and with other Federal agencies to minimize environmental insults which could occur from cadmium. Similarly, we are anxious to identify, perfect, and test alternative materials and processes for defense applications.

The purpose of this conference, therefore, is to try to provide consumers with a suitable selection of options to electrodeposited cadmium. This workshop could also provide the regulatory agencies, such as the U.S. Environmental Protection Agency, with an overview of the essentiality of cadmium to U.S. consumers.

Electrodeposited Cadmium may be absolutely essential in many applications and EPA and other regulatory bodies should recognize that possibility.

I expect that this workshop will provide us with an understanding of the currently available technology and hopefully provide the basis for estimating the best available technology in the 1980's and beyond. You have been reading more and more about the amendments to the Federal Water Pollution Control Act and the role that BAT will provide in the 1983 and 1985 time frame.

If,during the next few years,it becomes evident that the usage of electroplated cadmium decreases or changes on a national scale, a result that may, in part, be attributable to this workshop, then regulatory agencies responsible for restricting or changing the usage of other toxic substances may wish to sponsor similar workshops on these materials. As such, a workshop that brings together scientists and engineers to thoroughly discuss alternatives, who then proceed to adopt those alternatives, may be a promising mechanism for voluntary compliance as opposed to mandatory compliance. For example, we currently find ourselves in a mode of mandatory compliance with a Phase II type change to the Federal Water Pollution Control Act. Here we are going away from a guidelines type act to a "how to do it" type act on a much more voluminous scale.

---

* "Cadmium - Utilization, Environmental Impact, Materials and Processes Specifications, and Substitutes", Edward J. Dyckman, Defense Industrial Resources Support Office (DIRSO), June 1975.

The proceedings of this workshop, which will include not only the papers presented, but transcripts of all discussions held during the workshop, will be used by all elements of the Department of Defense in our effort to assess the various approaches to minimize the loss of cadmium to the environment.

Four of the 17 papers here this week are from the Department of Defense, and we are proud of that achievement.

Once again, we are very proud to be a part of these proceedings, and we are most sincere in our efforts to protect the environment and to protect our workers. We trust and pray that the week's outcome will be a series of positive approaches to meet both of those goals and, of course, your own individual goals.

Alternative Materials and Processes

Session I

Tuesday Morning 9:35

A NEW STRATEGY FOR CONTROLLING PRIORITY WATER POLLUTANTS

Dev Barnes
Ernst P. Hall
Effluent Guidelines Division
Office of Water Planning and Standards
Environmental Protection Agency
Washington, D.C. 20460

In June of 1976 the Environmental Protection Agency (EPA) entered into a consent agreement settling outstanding litigation by NRDC and others. This settlement can be characterized as having five major parts, one of which removed cadmium as well as lead and cyanide from the 307(a) toxics list as it then existed. This change allows us to approach the cadmium plating waste problem by considering not only toxicity but also balancing technology, economics, exposures and other factors as may be pertinent against the needs of the environment and society.

This consent agreement requires EPA, inter alia, to reevaluate and revise effluent limitations for 21 categories based on the best available technology economically achievable (BAT) considering the need to regulate 65 listed pollutants (priority pollutants) as well as conventional pollutants. One of these categories is electroplating and cadmium is one the 65 priority pollutants. Therefore we are committed to revising the cadmium discharge allowance for electroplating. Electroplating applies as a manufacturing unit process anywhere it is practiced and is not limited to independent or job shop platers.

The program of BAT revision for electroplating has only now begun and the technical and economic studies are to be completed by January 1, 1979. Revised regulations are to be promulgated by 1-1-80.

Because we are at such a preliminary stage of this study it is hazardous to make firm predictions of the nature and discharge limits in any final regulations. However, some possible scenarios for tight control of cadmium wastes may be appropriately discussed.

A NEW STRATEGY FOR CONTROLLING PRIORITY WATER POLLUTANTS

Ernst P. Hall, P.E.
U.S. Environmental Protection Agency
Effluent Guidelines Division (WH-552)
Washington, D.C. 20460

On June 7, 1976 the Environmental Protection Agency signed an agreement which settled four law suits brought against the Agency by the National Resources Defense Council and the Environmental Defense Fund. These suits were aimed at forcing the Agency to take action on and to expand the list of toxic substances to be regulated under Section 307(a) of the Federal Water Pollution Control Act (the Act) and to promulgate previously proposed pretreatment standards. In reaching a settlement, the Agency agreed; 1) to promulgate 307(a) standards for six pollutants on the 307(a) toxics list (aldrin-dieldrin, benzidine, endrin, PCBs, toxaphene and DDT); 2) to remove the remaining three materials from the 307(a) toxics list (mercury, cadmium and cyanide); 3) to complete rule-making of pretreatment standards which had been proposed for eight industrial categories; 4) to review and revise effluent limitations based on the best available technology (BAT) and new source standards for a list of 21 industrial categories, and 5) to revise or promulgate pretreatment standards for 21 industrial categories. In these final two steps, the Agency agreed to give special consideration to a list of 65 compounds or families of compounds which we commonly refer to as priority pollutants.

It is important to make clear a potential semantic problem when we discuss toxic pollutants or priority pollutants. Materials designated under section 307(a) of the Act are designated as toxic pollutants. Materials so designated require separate effluent standards to be established based primarily on their toxicity. The list of pollutants in the Settlement Agreement, while they may have toxic effects, have not all been formally designated as toxic materials under section 307(a). Rather they have been singled out for special study and investigation by the Agency for appropriate control under BAT and pretreatment authorities of the Act.

As I pointed out, the Settlement Agreement specified a list of 65 priority compounds and classes of compounds to be given special consideration in our studies. The list contains several classes of organic materials which must be expanded into sublists or specific representative compounds in order to remove ambiguity in our study effort. Thus, our working list actually contains a total of 129 chemicals (114 organics, 13 "heavy" metals, cyanide and asbestos). These are the priority pollutants for special consideration during the BAT review of the 21 industrial categories (a copy of this expanded listing is attached).

Under P.L. 92-500 and within the terms of the Settlement Agreement, there are a number of control options available to the Agency for dealing with industrial discharges of toxic or priority pollutants. The BAT standards and regulations called for under the Settlement Agreement represent the first step in dealing with such discharges. If it is determined that these technology based effluent standards are not adequate, the Agency may choose other control options. For instance, one option is to designate a material as a toxic pollutant under section 307(a). Under this section, standards more stringent than those established under BAT might be developed since 307(a) does not call for the detailed economic considerations required in the development of effluent limitations under sections 301 and 304. There are other options also in the area of water quality standards.

A variety of study efforts are involved in the implementation of the Settlement Agreement. As with our previous effluent guidelines efforts, we are conducting technical studies aimed at characterizing the various industries and their discharges as well as the technologies available for control and treatment of various pollutants. Also, as in our past efforts, we are conducting economic studies aimed at assessing the cost and economic impacts of various control options. However, there are two additional study efforts called for in the Settlement Agreement which make this program radically different from our earlier effluent guidelines efforts. These studies deal with the toxicity and exposure levels for the various priority pollutants and serve as the driving force behind the basic principles of integration and prioritization which we are attempting to incorporate into our strategy. In terms of toxicity, we will be looking at the effects of priority pollutants on aquatic life as well as potential harm to human health. Added to this will be information on the presence or absence of these pollutants in the Nation's waters and in industrial discharges. This combination of toxicity and exposure data will enable us to determine which pollutants and industrial categories are in need of regulation under BAT, new source and pretreatment authorities of the Act. In addition, it will serve as a guide to these and other authorities under P.L. 92-500 such as section 307(a). The use of studies is not intended to end at this point. To the extent we find the nature of a pollutant problem goes beyond industrial discharges, we can recommend appropriate actions (either regulatory or additional analysis) under other legislative authorities including Resource Conservation and Recovery Act, the Toxic Substance Act, and the Safe Drinking Water Act. It is our intent, because of the complexity of these studies, to place much of our early efforts on the screening of specific industrial discharges to identify those categories which truly merit regulation under the Settlement Agreement. Through this process we hope to narrow the number of materials and industrial categories with which we have to be concerned in the development of effluent limitations. Once this is done, we will proceed on an industry by industry basis to quantify more extensively the levels of discharge for various pollutants and the proper control techniques on which to base our regulations.

Obviously, this is a very ambitious and complex program. The thrust of the Settlement Agreement and the Act is to set in motion a continuing process for the identification of pollutant problems, analysis of these problems, selection of the proper regulatory mechanism and appropriate regulatory action. We are attempting to add one or two orders of magnitude of sophistication to environmental standards setting never before accomplished on the national level on such a broad scale. Many of the pollutants we are dealing with have never been studied before and as a matter of fact, analytical methods are still in the development stage for some of these materials.

Of particular interest to this meeting is the fact that cadmium and its compounds is one of the 65 materials and that electroplating, the most common manufacturing unit operation for applying cadmium to a base metal, is one of the 21 industries which must be studied. The stage therefore is set by a court order and consent agreement of 15 months ago, which deals directly with the problem we are considering in the several sessions of this meeting. The consent agreement schedule for electroplating requires that the Agency let a contract for technical studies and economic studies not later than October 1, 1977 and that the technical studies be completed in 12 months while an additional three months may be allowed for the completion of economic studies. The whole revision and rule-making process is scheduled to be completed not later than December 31, 1979 by the promulgation of revised BAT, new source and pretreatment standards. At this point in time, we are on schedule in this endeavor and have selected Hamilton Standard Division of United Technologies as the contractor for the electroplating technical study. I anticipate that our modus operandi on this project will be relatively similar to the approach used in the 16 preceeding BAT studies which have already been initiated. This includes the collection of a substantial amount of information from the industry itself, the sampling of a number of plants for determining the presence or absence of priority pollutants and more intensive studies of some of the industry concentrating on the priority pollutants found to be present and on the effectiveness of various technologies in removing these undesirable materials.

Because the project is in its infancy - officially it was to start last Saturday - I am not really able to tell you with certainty how it may come out, but I might suggest there are some things which we might want to examine closely and see if they will result in substantial reduction in the discharge of cadmium from electroplating.

> First, there is the possibility of requiring that wastes from cadmium plating be segregated and treated separately from any other electroplating wastes. This might have a number of advantageous effects such as reducing the amount of waste water which must be treated to remove cadmium and providing a more concentrated cadmium waste for treatment.
>
> A second technology which almost immediately comes to mind is to require multiple stage cascade rinsing controlled by electronic meters in order to reduce the amount of rinse water derived from the plating process. I am told for example that a six stage cascade rinse can provide the same level of product cleanliness as a single stage flowing rinse with about 1/1000 of the volumetric flow. Similar consideration in reducing the amount of process waste water from cleaning operations might need to be considered if those cleaning or rinsing operations result in the discharge of cadmium.
>
> The third obvious area for applying technology would be in the treatment of the greatly reduced volume of process waste water. The present BPT concept of neutralization and sedimentation most certainly will be looked at to see if some more advanced pollutant removal system will not be substantially more effective. It appears probable, for example, that a very simple treatment of lime and settle technology followed by filtration would result in a substantial reduction of metal content from the neutralization and sedimentation technologies now being considered at BPT. Additionally, more advanced but still well known technologies of sulfide precipitation followed

> by sedimentation and good filtration would be even more able to reduce the volumes of materials discharged. If we presume that advanced rinsing techniques are successful in reducing water flows, it may even be possible to apply more advanced pollution control techniques such as reverse osmosis or evaporation to further concentrate the cadmium salts and put them in such a concentrated form that it would be economic to recover and reuse them or convert them into a solid form and for environmentally safe disposal.

Please do not interpret this as telegraphing what EPA is going to require as BAT for cadmium plating. I have simply discussed some of the possible options which the Agency most certainly will consider as it work through all of the options and develops the most appropriate control considering all of the relevant factors for cadmium plating.

Thank you.

Alternative Materials and Processes

Sesstion I

Tuesday Morning 10:10

COST EFFECTIVENESS IN THE TREATMENT OF CADMIUM ELECTROPLATING WASTE

Kenneth J. Yost
Institute for Environmental Health
Purdue University
West Lafayette, Indiana 47907

Cadmium electroplating waste treatment, recovery, and "housekeeping" measures are surveyed. Capital and operating costs are given for waste treatment/recovery systems designed to reduce cadmium concentrations in plant effluent to levels ranging from 1.5 ppm down to .3 ppm with a water use factor of 4 gal/ft^2 of area "processed" (as defined in the EPA Development Document for the Electroplating Point Source Category). Waste treatment/recovery alternatives considered are restricted to those which have been proven effective in practice for cyanide plating baths. These include the conventional flow-through and batch chemical destruct methods (alkaline chlorination for cyanide removal followed by pH adjustment and settling of metallic solids), evaporative recovery, filtration, clarifier sludge centrifugation, and housekeeping practices such as waste segregation, drip tanks, still rinses, spill recovery, etc.

Results of laboratory studies of cadmium precipitation in segregated as well as mixed metal electroplating waste are presented. Among the variables shown to affect cadmium solubility/treatability at various pH's are the initial concentration of cadmium in segregated waste, the initial relative proportions of cadmium and other metals in mixed metal wastes, the duration of "second stage" cyanide treatment, and the amount of alkaline cleaner solution mixed with metallic waste. Some implications of these results for the design and operation of chemical destruct waste treatment systems are given.

Cost Effectiveness for Cadmium Waste Treatment in the Electroplating Industry

by

K.J. Yost
Purdue University

The purpose of this paper is to discuss results of a study performed in late 1975/early 1976 for the Environmental Protection Agency Office of Toxic Substances relating to Cd removal efficiencies for waste treatment systems as a function of cost. The study was designed to produce a sequence of waste treatment systems made up of readily available, "proven" components, which afforded progressively more complete Cd removal. A total of four systems were postulated, along with a variety of "Housekeeping" measures such as drip tanks, still rinses, 3-stage counterflow rinses, drip pans, and waste segregation.

The performances of each of the four systems were characterized in terms of Cd concentrations in system effluent; these range from 1.5 ppm down to 0.3 ppm Cd with water use factors ranging from 80 $1/m^2$ ($2 gal/ft^2$) area processed down to 60 $1/m^2$ ($1.5 gal/ft^2$). The corresponding Cd discharge factors range from 120 mg/m^2 area processed down to 18 mg/m^2 area processed.

The estimates of system performance were based upon in-depth studies of operating waste treatment systems in over thirty electroplating shops located throughout the eastern half of the U.S. These studies were sponsored by the MFF, NAMF, and NSF. Performance estimates were frankly intended to be conservative, i.e. the Cd levels in shop effluent just cited are intended to reflect what can reasonably be expected from these systems operating in a "typical" job shop setting. It is entirely possible, in fact highly likely, that these performance criteria could be exceeded by extraordinarily carefully managed, perhaps vendor nurtured, systems.

The hypothetical waste feeding the four waste treatment systems derives from a hypothetical Cd plating line consisted of caustic cleaner, acid pickel, plating and chromating steps, each followed by a rinse. The line is shown in Figure 1. For calculational purposes, water use was divided equally among the four processes.

The use of counterflow rinses, in the process of reducing water use, will of course result in a much more concentrated waste stream input to the four proposed treatment systems. Observations of waste treatment system performance in field suggest that reduction of water use, and associated waste concentrations, generally diminishes the treatability of plating waste. This diminishing of plating waste treatability as a function of waste concentration has also been noted in our laboratory studies, as indicated in Figure 2. Figure 3 suggest that a Cd-water solution does not exhibit this concentration effect. The implication seems to be that the concentration effect is a function of plating bath constituents and/or bath contaminants. Figure 4 exhibits the concentration effect for dilute Cu plating solutions.

Another point relating to our choice of water use factors; counterflow rinse flow rates for rinses following the process steps in the hypothetical Cd plating line were arrived at by multiplying the 160 l/m^2 area processed special by EPA for the metal finishing industry in the April 24, 1976, Federal Register by the ratio of flow rates observed for 3-stage counterflow rinses to those observed for single rinses in our field studies.

The four postulated Cd waste treatment systems are discussed below. They are identified as systems A, B, C, and D, respectively in the order of increasing treatment efficiencies.

Waste Treatment System A is specified in Figure 5 and Table 1. Costs are in 1975 dollars. It is anticipated that Cd concentration can be reduced to 1.5 ppm in system effluent with a water use factor of 80 l/m^2 area processed. This is essentially a flow-through chemical destruct system with 3-stage counterflow rinses after each process step, housekeeping provisions for the containment of spills (process tanks placed in containment sites with provision for directing spill waste for acid-alkali treatment) and drip tanks and still rinses after the plating and chromating steps. The specified area processed in Cd plating is relatively high, corresponding to 1500 ft^2/hr Cd plating. This adds up to 12,000 ft^2 Cd plating/8 hour work day (plating and chromating are defined by EPA as "steps" where treated area contributes to the area processed total). The relatively high Cd production figure is consistent with our contention that if preferentially strict effluent guidelines are adopted for Cd as now seems likely, Cd plating will be done by relatively fewer shops specializing in Cd plating. The specified cost of the system does not include the CN destruct unit which was the subject of a separate study for OTS. Tank sizes are based upon 12 hour retention time. The retention time for the specified treatment level (1.5 ppm) is more or less arbitrary and consultation with individuals (e.g. S. Gary, Dick Crain) in the waste treatment business. Labor costs for operating this system are estimated to be \$1.40/1000 ft^2 area processed; chemical costs are \$6.10/1000 ft^2 area processed; and sludge disposal costs are estimated to be 24C/1000 ft^2 area processed.

Waste Treatment System B is given in Figure 6 and Table 2. It is the same as System A but with an evaporation recovery unit in place of the cyanide waste treatment system and the drip tank and still rinse following the plating tank. The cost comparison with System A does not include capital saving associated with the deletion of the CN destruct unit. The addition of the evaporative recovery unit is expected to reduce Cd concentration in system effluent to 1.0 ppm, and reduce the water use factor of 2 gal/ft^2 to 1.5 gal/ft^2. Labor, chemicals and sludge disposal costs for this system are \$1.50/1000 ft^2 processed, \$4.10/1000 ft^2 processed, and .16/1000 ft^2 processed. The relatively "small" Cd reduction factor is associated with the containment of post-plating rinse by the evaporative recovery unit. Evaporative recovery units must recover cyanide to the point that no supplementary cyanide treatment is required. This was not the case for several of the units we have surveyed.

Waste Treatment System C is the same as System B with the addition of a filtration unit (with backup) to polish the Acid-Alkali clarifier effluent. The componant list is summarized in Table 3. Filtration units must be shown to be practicable for the plating industry where water use factors are low, and degree of waste concentration high, i.e. they must function without excessive blinding or degradation of filter membranes/materials. The filter specified here is of the leaf type with a vibrator to shake off dry cake. The filtration unit (with backup) is expected to reduce Cd concentration in system effluent from 1.0 ppm down to 0.5 ppm. Chemicals and sludge disposal costs for this system are assumed to be the same as for System B. Labor costs are estimated to rise from \$2.10/1000 ft^2 processed to \$2.48/1000 ft^2 area processed. The increase is associated with maintenance of the filtration unit.

Waste Treatment System D is summarized in Figure 7 and Table 4. It is identical to System C but with three tanks for batch treatment of acid-alkali waste. Treatment tanks are sized to allow for 24 hour detention time. Each treatment tank is agitated at the time treatment chemicals are added by paddle mixers with 2.5 HP turbine type motors. Batch treatment of the acid-alkali waste is expected to reduce Cd concentration in system effluent from .8 ppm down to .3 ppm. Chemicals and sludge disposal costs are assumed to be the same with System D as with System C. Labor costs, however, are estimated to rise from \$2.45/1000 ft^2 are processed to \$5.60/1000 ft^2 area processed. The increase in labor costs are associated with the maintenance and monitoring associated with the batch treatment system. Sufficient floor space must be available for treatment tanks. This may be a substantial problem for urban shops. Recessed floor tanks may be a partial answer to this problem for shop occupying ground floor area in urban building.

Chemicals and labor costs for the four proposed systems were in part derived from data collected on our plant surveys. Table 5 gives a summary of some of these data. Tables 6 and 7 summarize labor, chemicals and sludge disposal costs; and water use factors, Cd discharge (mg/m^2 area processed), and Cd discharge concentrations for the four treatment systems.

Figure #	Caption
1	Hypothetical Cadmium Plating Line
2	Apparent Solubility of Cadmium as a Function of pH in a Plating Solution Diluted to 1000, 500, and 200 ppm Cadmium. Shop # 4.
3	Apparent Solubility of Cadmium as a Function of pH in Cadmium Chloride Solutions. Samples Were pH Adjusted and Allowed to Settle for One Hour, then the pH of Each Sample was Remeasured and the Sample Filtered.
4	Apparent Solubility of Copper as a Function of pH in a Plating Solution Diluted to 1000, 500, 200, and 50 ppm Copper. Shop #8.
5	System A Schematic
6	System B/C Schematic
7	System D Schematic

Table #	Caption
1	System A Component List
2	System B Component List
3	System C Component List
4	System D Component List
5	Waste Treatment, Labor, and Chemical Costs.
6	Estimated Operating Costs for Proposed Waste Treatment Systems.
7	Expected Performance of Proposed Waste Treatment Systems.

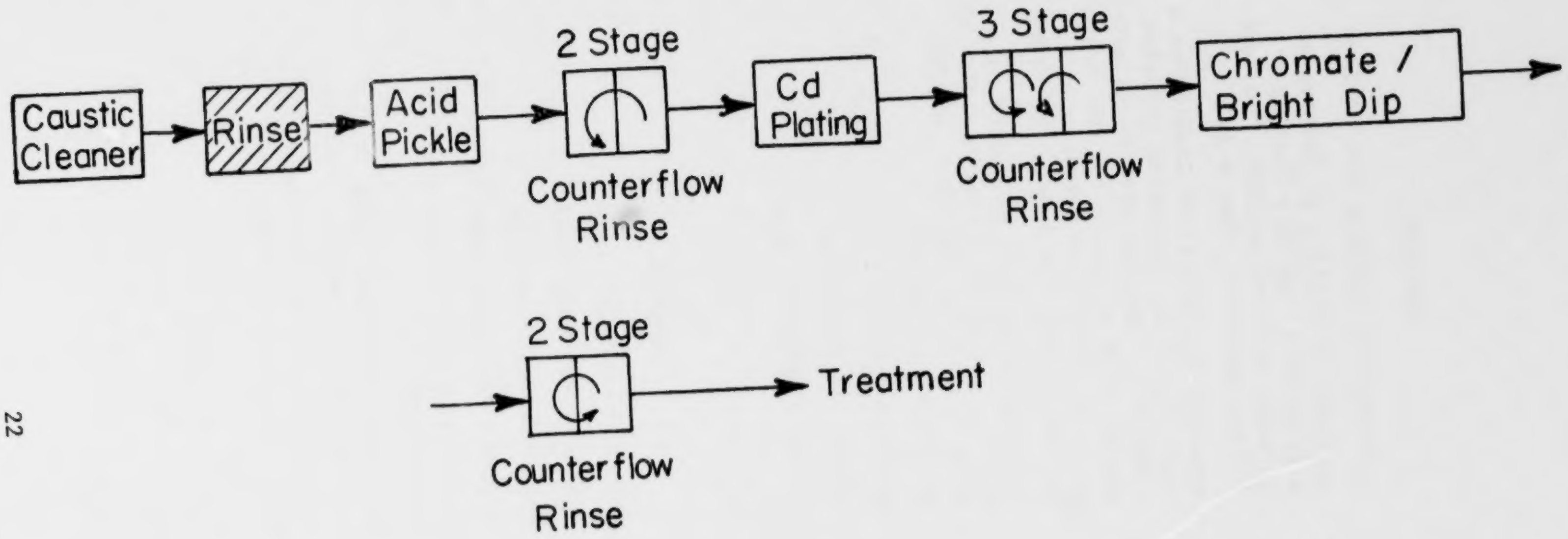


Figure 1: Hypothetical Cadmium Plating Line.

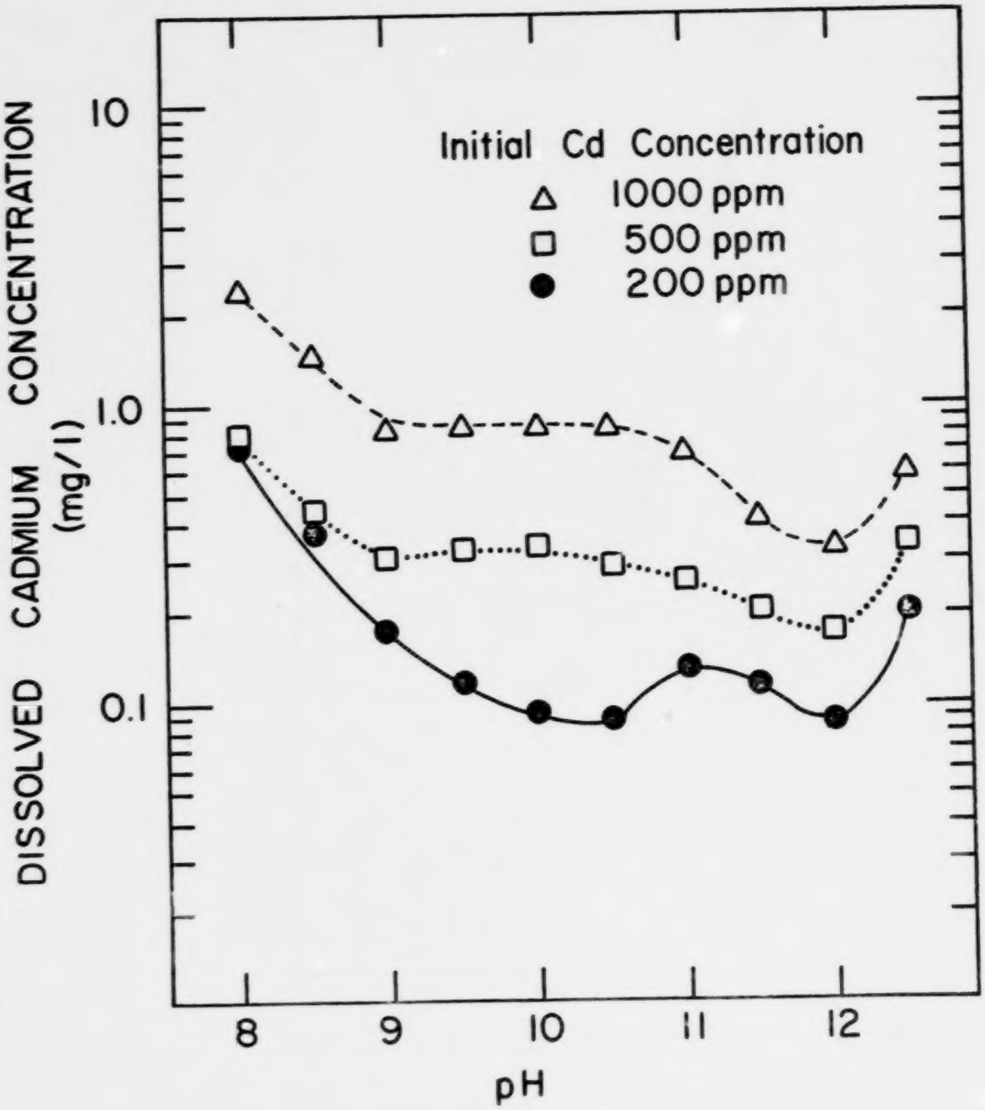


Figure 2: Apparent Solubility of Cadmium as a Function of pH in Cadmium of pH in a Plating Solution Diluted to 1000, 500, and 200 ppm Cadmium. Shop #4.

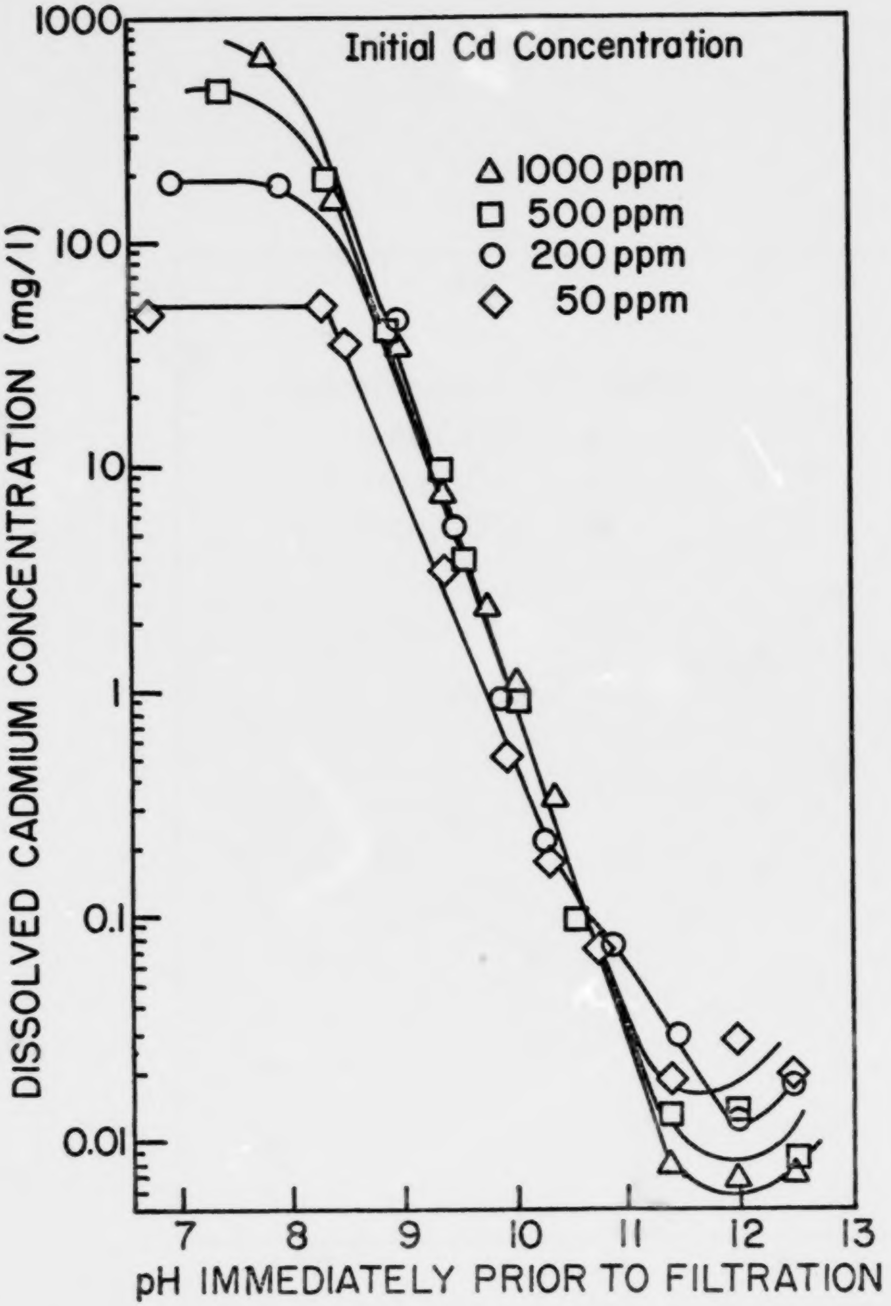


Figure 3: Apparent Solubility of Cadmium as a Function of pH in Cadmium Chloride Solutions. Samples Were pH Adjusted and Allowed to Settle for One Hour, then the pH of Each Sample was Remeasured and the Sample Filtered.

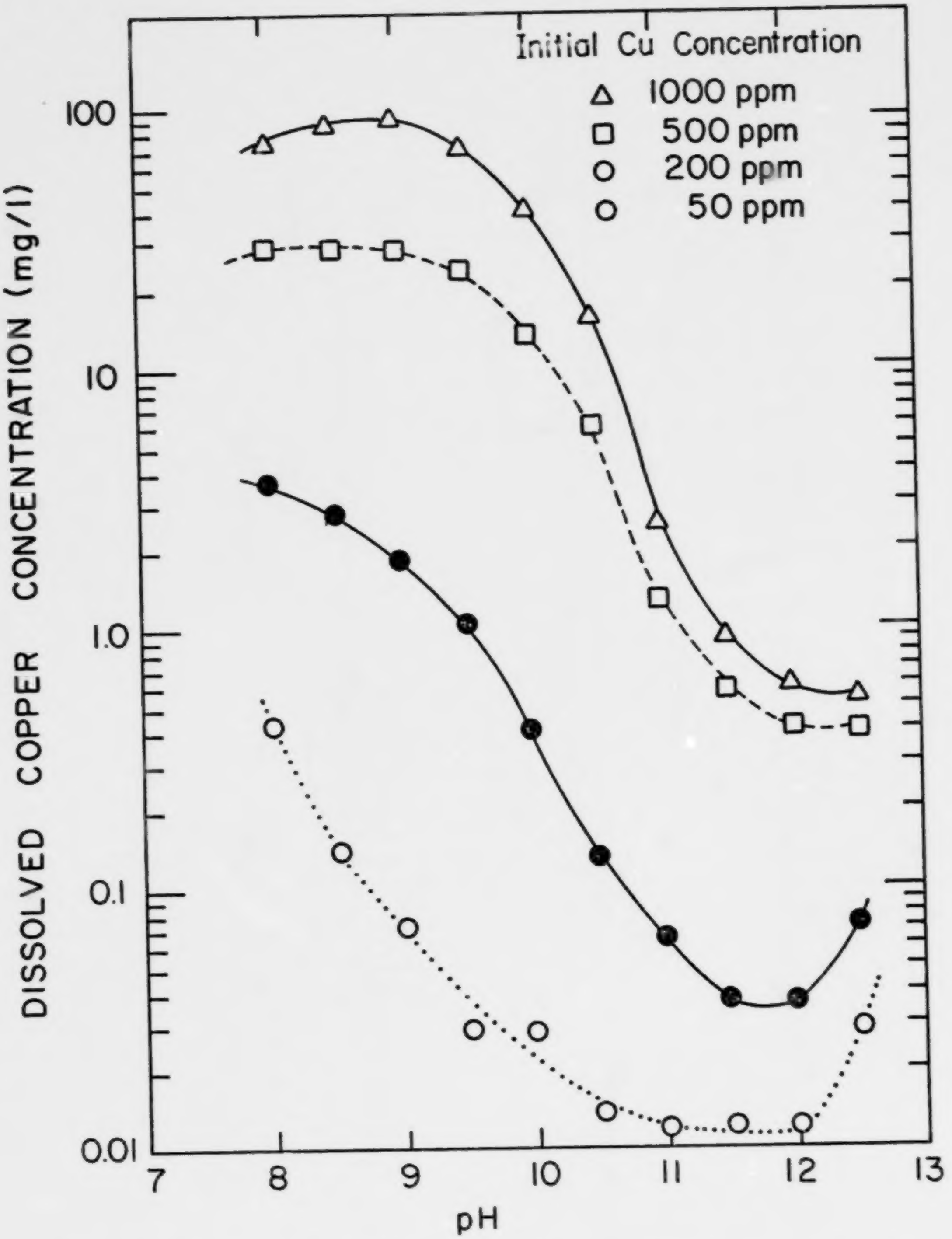


Figure 4: Apparent Solubility of Copper as a Function of pH in a Plating Solution Diluted to 1000, 500, 200, and 50 ppm Copper. Shop #8.

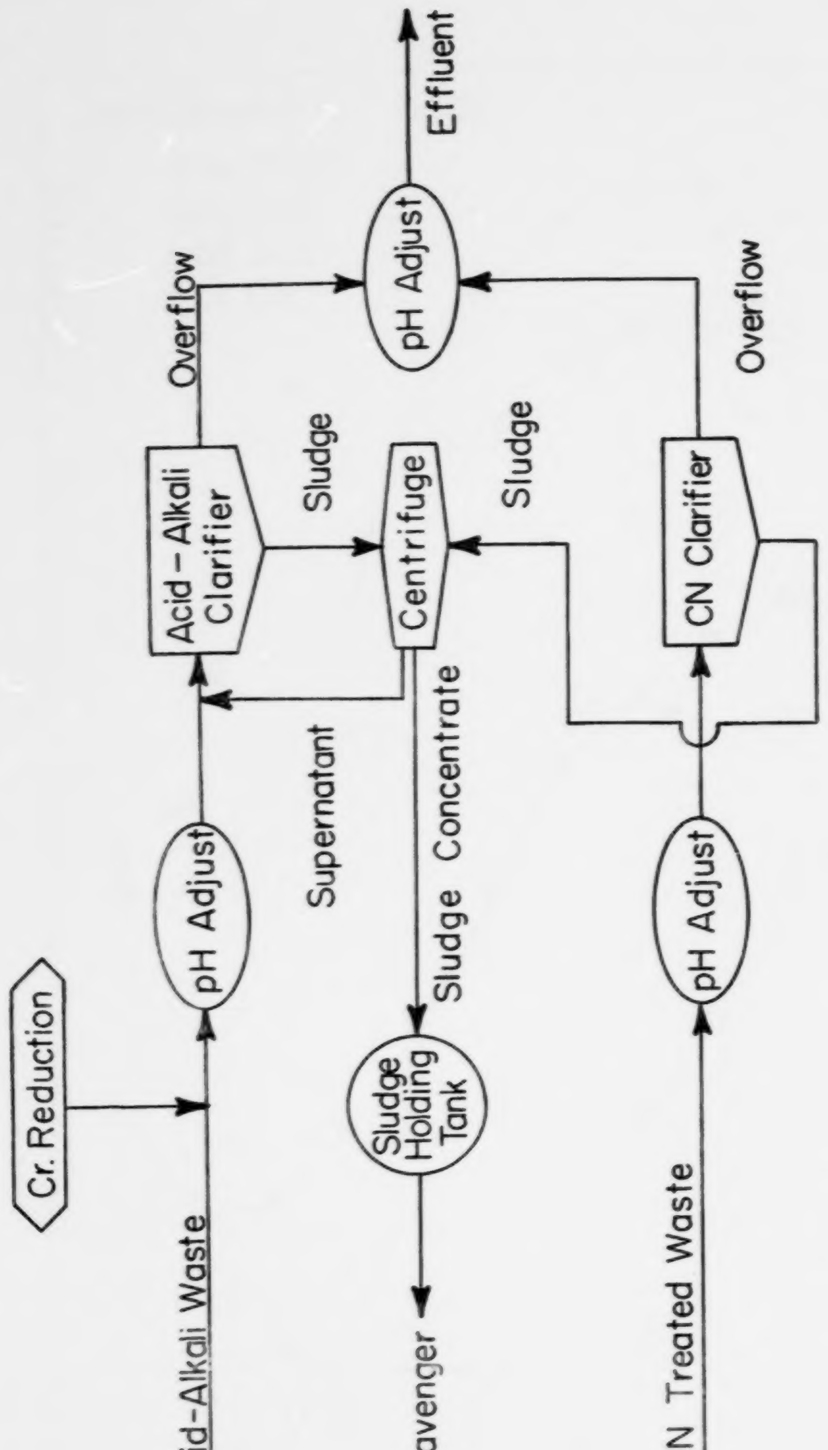


Figure 5: System A Schematic

Table 1:

System A - Flow-Through Chemical Destruct System With Housekeeping Provisions for the Containment of Spills. Drip tanks and still rinses after the plating and chromate baths. Three-stage counter flow rinses for all steps in plating line.

	Components	Size	Capital Costs ($)
1)	2 pH Adjust Tanks	500 gal.	1,600
2)	Centrifuge	3 gal/hr of 20% solids sludge	6,000
3)	2 pH Controllers	----	5,600
4)	Final pH Adjust Tank	1,000 gal	1,600
5)	Acid-Alkali Waste Clarifier (rubber lined)	18,000 gal/1,000 ft^2 processed/hr	18,400/1,000 ft^2 processed/hr
6)	Cyanide Waste Clarifier (painted)	6,000 gal/1,000 ft^2 processed/hr	4,100/1,000 ft^2 processed/hr
7)	Chrome Reduction Unit	2,000 gal/hr	13,600 (with ORP)
8)	Cyanide Destruct Unit	2,000 gal/hr	Not included
9)	Acid for Caustic Tanks for pH Adjust	500 gal.	1,600
10)	Engineering costs for 3,000 ft^2 Area Processed in Cd Plating/hr. (10% capital cost does not include CN treatment capital)		9,750
	Total (3,000 ft^2 Area Processed in Cd plating/hr - not including CN treatment capital costs)		107,250

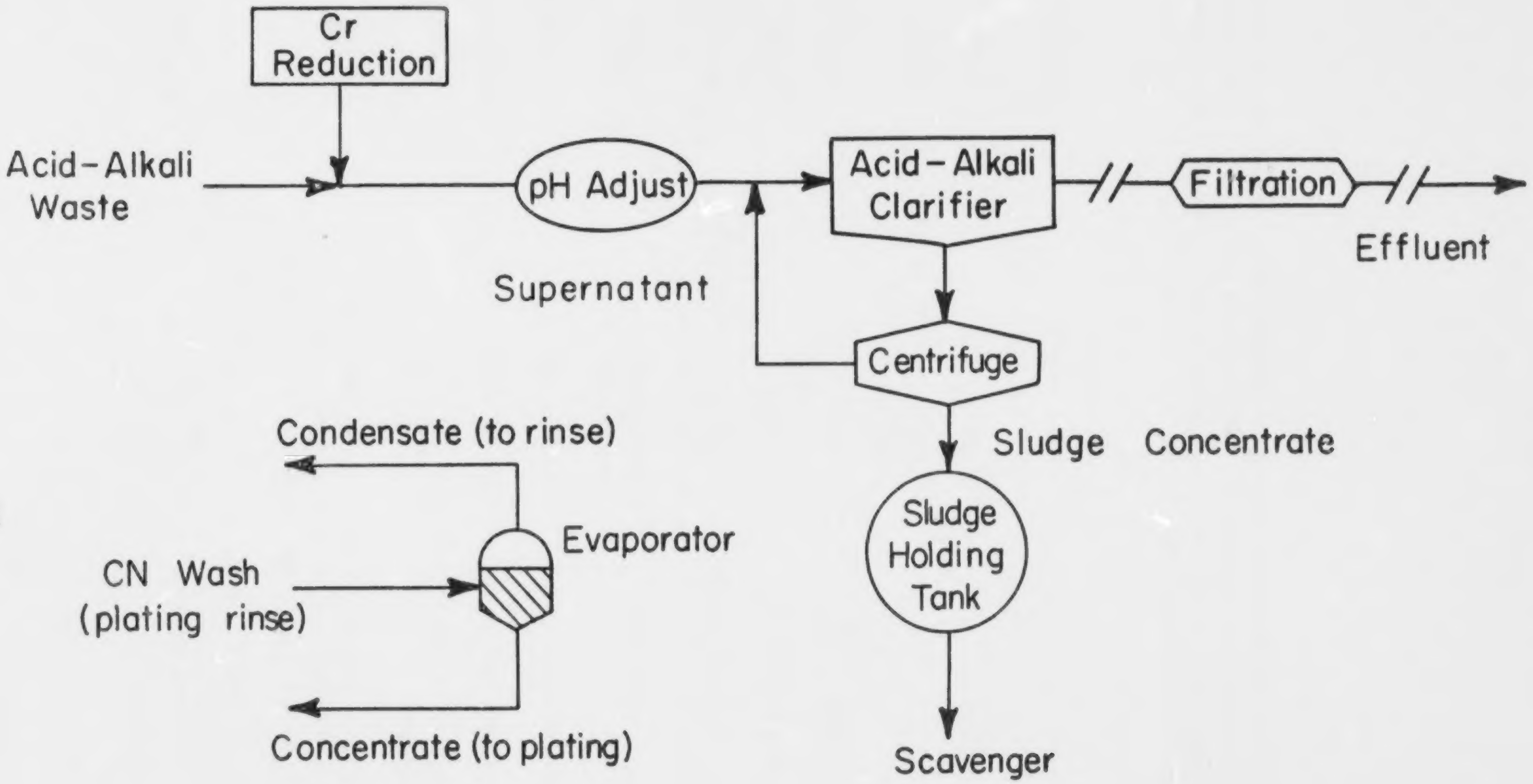


Figure 6: System B/C Schematic

Table 2:

System B - Same as System A but with an evaporative recovery unit in place of the cyanide waste treatment system and the drip tank and still rinse following the plating tank.

	Components	Size	Capital Costs ($)
1)	pH Adjust Tank	500 gal	1,000
2)	Centrifuge	3 gal/hr of 20% solids sludge	6,000
3)	pH Controller	----	2,800
4)	Acid Alkali Waste Clarifier (rubber lined)	18,000 gal/1,000 ft^2 processed/hr	18,400/1,000 ft^2 processed/hr
5)	Chrome Reduction Unit	2,000 gal/hr	13,600 (with ORP)
6)	Evaporative Recovery Unit	100 gal/hr	33,000
7)	Engineering Costs for 3,000 ft^2 Area Processed in Cd Plating/hr (10% of capital)		11,200
	Total (for 3,000 ft^2 Area Processed in Cd Plating/hr)		122,900

Table 3:

System C - Same as System B with the addition of a filtration unit (with backup) to polish the Acid-Alkali Clarifier Effluent.

	Components	Size	Capital Costs ($)
1)	System B	- - - - -	111,600 for 3,000 ft^2 area processed/hr in Cd plating
2)	2 Filtering Units	- - - - -	24,000
3)	Engineering Costs for 3,000 ft^2 Area Processed in Cd Plating/hr (10% of capital)		13,600
	Total (3,000 ft^2 Area Processed in Cd plating/hr)		149,200

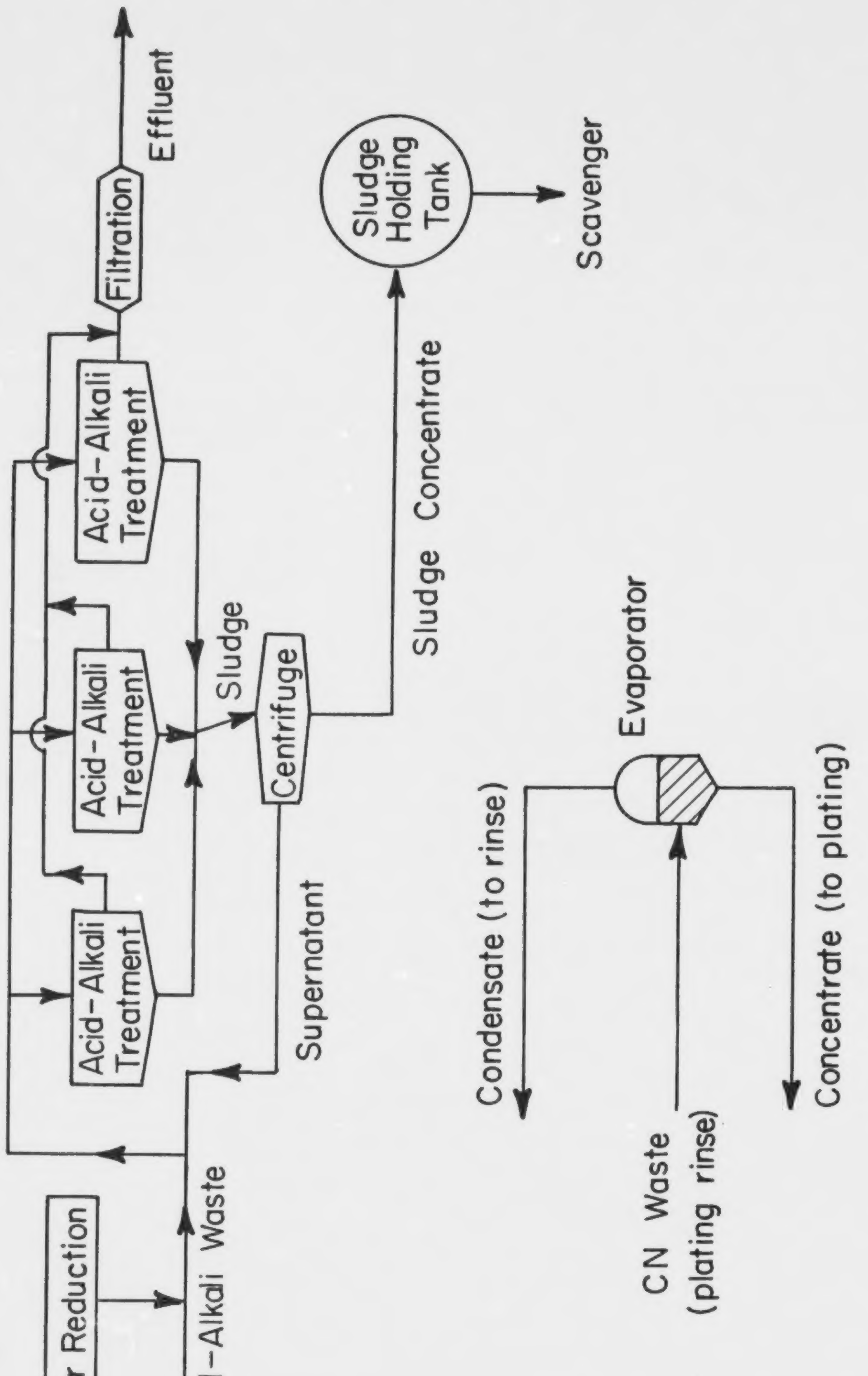


Figure 7: System D Schematic

Table 4:

System D - Same as System C but with three clarifiers for batch treatment of Acid-Alkali Waste. Clarifiers are sized to allow for 24 hour detention time.

	Components	Size	Capital Costs ($)
1)	System C less Acid-Alkali Clarifier	- - - - -	80,400
2)	3 Acid-Alkali Settling Tanks (rubber lined)	1,500 gal/1,000 ft^2 processed/day	129,600 for 3,000 ft^2 area processed/hr in Cd plating
3)	4 - 5HP Turbine Paddle Mixers (1 back up)		12,000
4)	Engineering Costs (10% of capital)		22,200
	Total (30,000 ft^2 Area Processed in Cd plating/day)		244,200

Table 5: Waste Treatment, Labor, and Chemical Costs.

Shop	Labor ($/1000 ft^2 Processed)	Chemicals ($/1000 ft^2 Processed)	System
#2	3.70	3.80	Batch
#3	2.18	4.10	Continous
#4	0.32	.15	Continous
#6	0.23	.54	Continous
#8	0.79	1.10	Continous
#10	0.79	1.20	Continous
#11	0.02	.86	Continous
#14	5.84	16.0	Continous (Batch for Cr & CN)
#17	4.42	9.1	Continous
#19	0.25	.10	Continous

Table 6: Estimated Operating Costs for Proposed Waste Treatment Systems.

System	Labor ($/1000 ft^2 Processed)	Chemicals ($/1000 ft^2 Processed)	Sludge Disposal ($/1000 ft^2 Processed)
A	1.40	6.10	.24
B	2.10	4.10	.16
C	2.45	4.10	.16
D	5.60	4.10	.16

Table 7: Expected Performance of Proposed Waste Treatment Systems.

Waste Treatment	Water Use Factor (1/m²)	Cd Discharge/Area Processed in Cd Plating (mg/m²)	Cd Concentration in Clarifier Effluent (mg/1)
System A	80	120	1.5
System B	60	60	1.0
System C	60	30	.5
System D	60	18	.3
EPA Effluent Guidelines Proposed Standard-Existing Source	160	36	.6
EPA Effluent Guidelines Proposed Standard-New Source	80	18	.6

COST EFFECTIVENESS IN THE TREATMENT OF CADMIUM ELECTROPLATING WASTE

DISCUSSION PERIOD

SPEAKER: I assume you did all your work with alkaline cadmium solutions.

DR. YOST: Yes.

SPEAKER: Did you do any work with cadmium acid solutions?

DR. YOST: We have done the solubility work, but no field studies of acid.

SPEAKER: Has anybody at all?

DR. YOST: We have no field data. We have seen in the lab that we don't notice this concentration effect. We have done some laboratory work with acid copper and find that we do not see the concentration effect with acid copper solution, but that we do see it with the cyanide copper. I suspect that the situation would be the same with cadmium.

MR. POPE: Dick Pope, the Weatherhead Company. In your experience, do you think it is possible to meet a .03 parts per million effluent limit on cadmium?

DR. YOST: My personal opinion is that this requires a closed loop. There is no point in tracking down to those levels. Nobody could handle them.

MR. POPE: Would this mean that you don't have any effluents?

DR. YOST: I think you can go to expensive closed loop systems. I suppose you can throw back on your pickle rinse, some of your chromates, your plating rinse. I don't know what to do about your cost.

MR. KRAFT: Jerry Kraft, Kraft Chemical. I wonder if you would summarize your original work on the effect of cadmium in the sediment and whatever effect that had on its life cycle.

DR. YOST: Basically, cadmium introduced into aquatic systems is quickly precipitated and deposited into bottom sediment. We have found that as far as edible fish species are concerned, even fish that are obtained from heavily cadmium-contaminated areas do not show alarmingly high cadmium concentrations in their edible portions. There is Cd concentration in the fish liver and kidney.

DR. YOST: We find that, generally, cadmium lies relatively dormant in the sediment once it is introduced into an aquatic system. It is not like methylated mercury or something of that nature.

We found cadmium concentration in sludge as high as 1,000 parts per million, and the background in that area is about two to three tenths.

SPEAKER: It was hard to tell from the chart, the total cost of the weight measurements, say, for 10,000 square feet of cadmium; was it the total of those figures you had on the slide there?

DR. YOST: Yes, that was the bottom figure.

SPEAKER: Can one assume in the next to last table that the higher labor cost would be the one that would be the less likely to pollute the water streams?

DR. YOST: Yes, because the more complex and costly systems require much closer monitoring and maintenance in general.

SPEAKER: But the guy who has the labor cost of only 25¢ an hour, what is he doing?

DR. YOST: As little as he can.

DR. YOST: This survey was prompted by our interest in the job shop component of the plating industry. It is this component that is going to be most totally affected by the final EPA effluent guidelines.

SPEAKER: Going back to your solubility curves, you are showing a higher concentration which is less efficient in bringing that down because you included chelating agents. Jumping over to systems that you proposed for waste treatment, do you see a problem assuming higher concentrations? How effective are these systems? Down to what concentrations do you get the cadmium?

DR. YOST: I guess I will have to dodge that one. I think the jury is still out. For this particular study, we did specify a segregation of the cadmium waste, which will do away with another effect which we have seen. When you mix cadmiumzinc that seems to elevate the apparent solubilities of each metal. But I think it would probably meet these limits, even with that effect.

SPEAKER: On those studies, were you treating cadmium and chrome at the same time?

DR. YOST: Yes.

SPEAKER: We are not just talking cadmium then?

DR. YOST: No. The costs that were associated are related to that hypothetical plating line which has the chrome destruct system as part of it.

The Cd line had a chromating step, and we had in those costs included a chrome reduction capability.

Alternative Materials and Processes

Session I

Tuesday Morning 10:45

SURFACE ALLOYING BY ION IMPLANTATION: AN ALTERNATIVE TO CADMIUM ELECTROPLATING

B. D. Sartwell
F. X. McCawley
College Park Metallurgy Research Center
Bureau of Mines, U.S. Department of the Interior
College Park, Maryland 20740

The Bureau of Mines is conducting research with the goal of conserving critical alloying elements. This research includes studies to develop a new class of corrosion--resistant alloys that are fabricated by the implantation of energetic metallic ions into either an iron or low-alloy substrate. The advantages of using ion implantation over electrolytic plating are (1) the alloyed surface region, extending to depths of up to 100 nm, is an integral part of the substrate, thereby eliminating problems such as interfacial weakness and dimension change, (2) ion implanation produces no environmentally unacceptable byproducts that would contribute to air or water pollution, and (3) the amount of electrical power required to produce an equivalent corrosion- resistant surface is estimated as being from 4 to 10 times less than required for conventional electroplating techniques.

Surface stainless steels have been fabricated by implantation of low-energy chromium and nickel ions into iron. The quantity of chromium and nickel used was approximately 2 ug/cm^2 of the substrate. These surface alloys have been compared to cadmium - plated steel in corrosion tests involving exposure in several metallurgical process environments. Results have shown that the relative corrosion rates are comparable. Preliminary corrosion tests of iron implanted with cadmium ions have shown that surface protection can be provided using ion implantation.

Preceding page blank

SURFACE ALLOYING BY ION IMPLANTATION: AN ALTERNATIVE TO CADMIUM ELECTROPLATING

by

B. D. Sartwell
College Park Metallurgy Research Center
Bureau of Mines, U.S. Department of the Interior
College Park, Maryland 20740

Abstract

The Bureau of Mines has fabricated a new class of alloys by implantation of low-energy metal ions into the surface regions of iron to doses ranging from 1.0 to 4.0×10^{16} ions/cm^2. The alloy distribution as a function of depth (depth profile) has been determined for polycrystalline iron samples implanted with either 25-keV chromium or nickel ions, and the results have been compared with theoretical predictions. The resistance of these "surface alloys" to environmental attack has been evaluated both by determining their anodic polarization behavior under potentiostatic conditions and by determining their gaseous oxidation characteristics. Results of the electrochemical studies have shown that the general corrosion resistances of the surface alloys were comparable to those of nominally equivalent bulk alloys and that the pitting-corrosion resistances for the surface alloys were superior to that for iron, although generally not as good as those for most equivalent bulk alloys. Gaseous oxidation studies have shown that surface and bulk iron-chromium alloys exhibit essentially identical oxidation kinetics, with a much higher rate of oxidation observed for iron. In both the aqueous corrosion and gaseous oxidation studies, the quantity of the alloying element used to fabricate the surface alloys was six to seven orders of magnitude less than that required to fabricate equivalent bulk alloys.

Introduction

To ensure the United States an adequate supply of critical materials, the Bureau of Mines is conducting research to develop new, substitute corrosion-resistant materials. The formation of alloyed regions near the surfaces of metals using ion implantation is being investigated as a means of providing corrosion resistance while realizing a substantial reduction in the consumption of expensive alloying materials that are in limited supply. Ion implantation is a nonpolluting process and, therefore, should also be investigated as a potential substitute for standard electroplating processes.

In this paper, the corrosion behavior of the surface alloys formed by ion implantation will not be directly compared to that of cadmium-electroplated steel. Comparisons will be made, however, between the surface alloys and nominally equivalent bulk Fe-Cr and Fe-Ni alloys which are known to be highly resistant to corrosive attack. It is believed that if the surface alloys can be shown to possess corrosion resistance comparable to the bulk alloys while using orders of magnitude less of the alloying element, the surface-alloying process could be a viable alternative to cadmium electroplating

Since its inception, the surface-alloying program at the Bureau of Mines has been divided into three interrelated components: (1) the development of the technology for the fabrication or production of surface alloys, (2) the investigation of the physical properties of surface alloys, and (3) the study of the aqueous and gaseous corrosion characteristics of surface alloys compared to those of conventional bulk alloys. The development of the fabrication technology has involved the design and construction of two metal-ion implantation systems. Using these systems, investigations have been conducted to determine the rate of production of surface-alloyed material, what types of metal ions can be implanted, and what size and shapes of material can be surface-alloyed. The study of the physical properties of the surface alloys has principally involved determining the specific alloy concentration as a function of depth (depth profile) and the effects of heat treatment on these profiles. Future work in this area will be addressed to determining the alloy phases formed, the number and types of defects produced in the substrate lattice by the implantation process, and the effects of friction and wear on the surface alloys. Corrosion characteristics of surface alloys have been investigated in both aqueous and gaseous environments by comparing the anodic polarization behavior and gaseous oxidation kinetics of surface alloys to those of nominally equivalent bulk alloys. Preliminary studies have also been conducted on determining the galvanic corrosion and stress-corrosion-cracking behavior of surface-alloyed material.

Summary of Ion Implantation Theory

Ion implantation involves the injection of energetic ions into a solid material. As ions penetrate a target material, they lose energy through collisions with the target atoms, eventually coming to rest at substitutional or interstitial lattice sites. The slowing-down process for the ions is considered mathematically as a statistical process, and the theories that have been developed to describe this process generally predict that the final distribution of the implanted atoms will resemble a Gaussian distribution (1). Figure 1 shows a typical Gaussian distribution for low-energy ions implanted into an amorphous material. The final concentration of the implanted species is plotted as the ratio of the concentration, $N(X)$, at a depth, X, to the maximum concentration, N_p. The two parameters that describe the

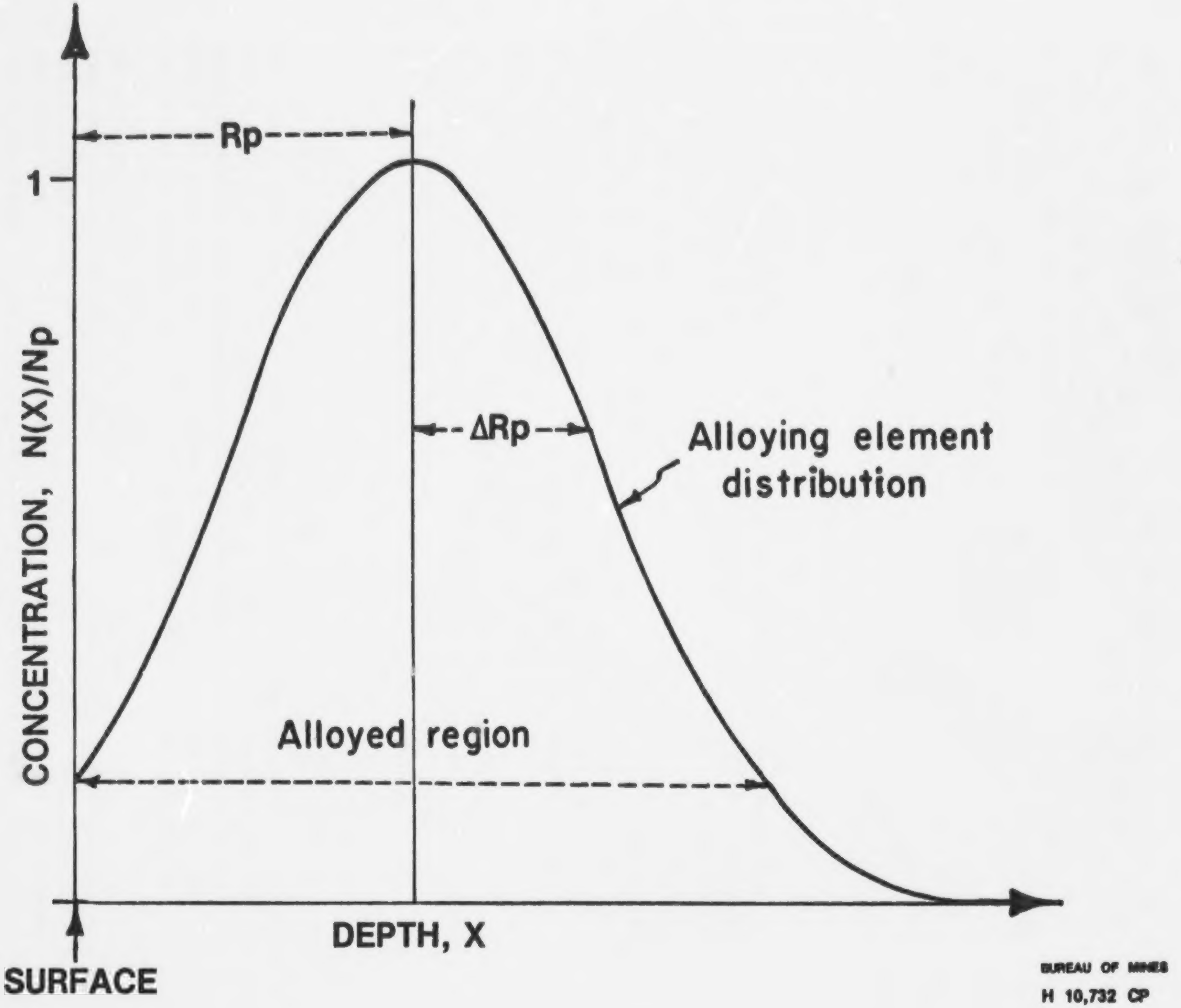


Figure 1. - Typical Gaussian distribution for low-energy ions implanted into an amorphous material.

distribution are R_p, the "mean range" or "mean depth of penetration" of the ions, and ΔR_p, the standard deviation of the distribution, sometimes referred to as the "range straggle."

The parameter that is normally used to describe the concentration of implanted atoms is the dose, D, the number of ions per square centimeter implanted into the substrate material. However, in order to compare surface alloy to bulk alloy systems, a designation for the surface alloys has been obtained by averaging the concentration of the implanted species over the region of the substrate extending from the surface to a depth, R_t, that would include 95% of the implanted species. This depth was determined experimentally for each alloy system that was fabricated. The average concentration, N, of the implanted species is calculated from $N = D/R_t$. The alloy designation is then Fe-C(s)I, where $C = N/8.5 \times 10^{22}$ for iron, and I is the implanted element.

Experimental Techniques

This section describes the experimental techniques used for the fabrication of the surface alloys and for the study of the corrosion characteristics of the surface alloys. Part I of this section discusses the method used to prepare samples for either ion implantation or for electrochemical and oxidation studies, Part II describes the ion implantation system used to fabricate the surface alloys, and Parts III and IV discuss the technique used in the anodic polarization and oxidation research, respectively.

I. The iron samples that were used in the corrosion studies and as substrate metal in the fabrication of the surface alloys were cut from high-purity (99.95%), cold-rolled iron sheet pruchased from the Materials Research Corporation.[1] The bulk Fe-Cr alloys used in the corrosion studies were fabricated by the Bureau of Mines, Albany Metallurgy Research Center. Other metals and alloys used in the electrochemical studies included high-purity nickel (99.5%) obtained from International Nickel Company, type-9 nickel steel obtained from the U.S. Steel Corporation, and a maraging steel (Vascomax-250) obtained from Teledyne Metals.

Preparation of the nickel, type-9 steel, and Vascomax-250 for the electrochemical studies consisted of mechanical polishing through 600 grit, cleaning with acetone and methanol, rinsing with 18-megohm water, and drying in ultra-high-purity (UHP) nitrogen.

Preparation of the iron and the Fe-Cr alloys was more extensive. This consisted of mechanical polishing through 600 grit, degreasing with acetone and methanol, heat-treating at 600° C for 2 hours in an argon atmosphere, and then a rapid water quench. To remove the thick scale resulting from the heat treatment, the samples were pickled in 20 vol-pct H_2SO_4, rinsed with 18-megohm water, and then dried with UHP nitrogen. Samples were then individually electropolished in a 400-ml solution of a 9:1 mixture of glacial acetic to 70 vol-pct perchloric acid. Following electropolishing, the samples were rinsed with 18-megohm water, dried in a stream of UHP nitrogen, and then mounted in the ion implantation system, the oxidation chamber, or the electrochemical cell, depending on the type of test to be performed.

---

[1] Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

II. The surface alloys used for the corrosion and oxidation studies were fabricated in the metal-ion implantation system shown schematically in figure 2. The principle of operation is as follows: a solid metallic compound (for example, $CrCl_3$) called the "charge" is placed in a short section of stainless steel tubing. During operation, this charge is inserted in the ion source where the compound is vaporized and ionized. The ions are "pulled" from the source by a negatively charged extractor electrode, focused into an ion beam by the focusing electrode, and then accelereated to the desired energy by the accelerating electrodes. The ion beams are analyzed according to the charge-to-mass ratio by the beam-analyzing magnet, providing fcr a high-purity beam of the metal ions entering the sample chamber. The LN_2-cooled section of beamline is designed to trap residual gases, such as chlorine, silicon, and hydrocarbons, generated either by the ion source or the vacuum pumping systems and to prevent them from entering the sample chamber and contaminating the surfaces of the samples.

The fabrication chamber is constructed of stainless steel with metal-seal flanges and pumped with a 110-liter-per-second ion pump capable of evacuating the chamber to a base pressure of 1×10^{-8} torr. The metal samples intended for implantation are mounted on a carrousel, with a diameter of 14 cm, able to accommodate either twelve 2.5-cm-diameter samples or twenty-four 1.25-cm-diameter samples. The carrousel is insulated from ground and connected to a current integrator that measures the total amount of ion beam charge incident on the samples. From the value of the measured charge, the ion dose, D, expressed in ions per square centimeter, could be calculated. There are, however, several uncertainties involved in the measurement of D in this manner. Therefore, the necessary quantitative determinations of the total ion doses and also of any surface contaminants introduced by the implantation process were obtained by proton-excited X-ray analysis (PEX) (2).

III. The aqueous corrosion behavior of the surface alloys was evaluated electrochemically under anodic polarization conditions in a 0.15N boric acid solution (20.6 g/equivalent weight) containing 0.4 wt-pct NaCl (2,400 ppm Cl^-) and buffered to a pH of 8.5 with the

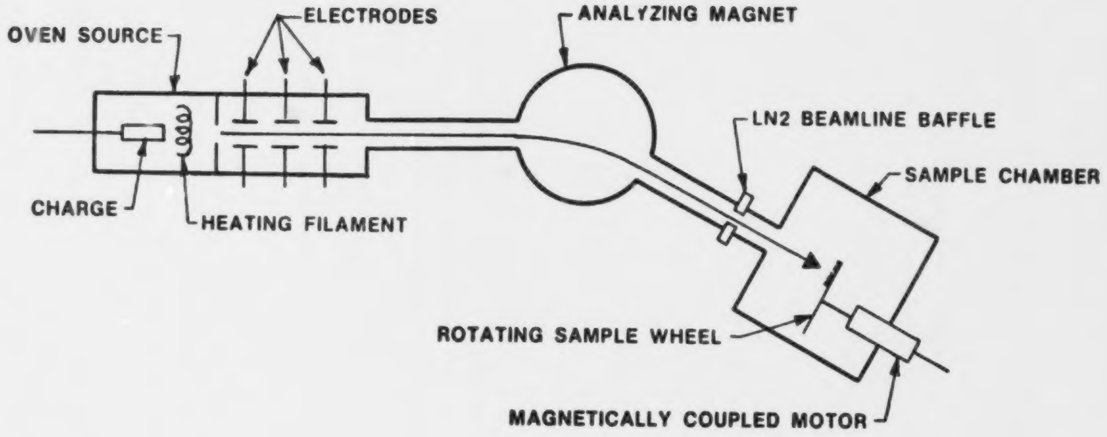


Figure 2. - Simplified schematic of Bureau of Mines metal-ion implantation system.

addition of 0.15N $Na_2B_4O_4 \cdot 10H_2O$ (5.5:1) (179.1 g/equivalent weight). The solution was prepared using reagent-grade chemicals mixed in 18-megohm water and was stored in a specially designed reservoir that kept the solution free of atmospheric contaminants and provided for direct transfer of the solution to the electrochemical cells.

The polarization measurements were conducted in a modified Greene-type (3) electrochemical cell that had been thoroughly cleaned with boiling HNO_3 and subsequently steamed with boiling 18-megohm water. This cell, including the modifications, is shown schematically in figure 3. Each cell consisted of a platinum counter-electrode, a saturated calomel reference electrode, and the working electrode (i.e., either a surface alloy, iron, or a bulk alloy). The working electrode was mounted in a compression holder that, for the surface alloys, isolated the nonimplanted regions of the sample from the solution. High-purity helium (99.9%) entered the gas inlet and stirred the solution in front of the working electrode in order to minimize diffusion control of the reactions. The saturated calomel reference electrode (SCE) was isolated using a Luggin-Haber probe. The potential of the working electrode was controlled with a Wenking 70TSI potentiostat and a Wenking VSC72 voltage scan generator. Anodic currents were measured with a Keithley 165 multimeter and recorded on an XY recorder.

The anodic polarization measurements were performed identically for iron, the bulk alloys, and the surface alloys. Prior to beginning the potential scan, the metal sample was cathodically reduced using the Wenking potentiostat in the galvanostatic mode. A cathodic current density of 5×10^{-4} amp/cm^2 was used to reduce the air-formed oxide films on the metal surfaces. The samples were then allowed to achieve a steady-state open-circuit rest potential (E_R) for 10 to 15 minutes, following which the anodic polarization test was initiated at -100 mV with respect to E_R with the potential scanned at a rate of 10 mV/min.

IV. The procedure used to determine the oxidation kinetics using PEX has been extensively discussed elsewhere (4), and only a brief description is given here. The sample to be oxidized was mounted in the ultra-high-vacuum PEX analysis chamber and was heated radiatively to the desired oxidation temperature of 300° C by a tungsten filament. At an ambient vacuum chamber background pressure of $<1 \times 10^{-8}$ torr, research-grade-purity oxygen (10 ppm total impurities) was leaked into the vacuum chamber, through a sapphire seal leak-valve, to a pressure of 4×10^{-6} torr in less than 2 seconds. Oxidation times ranged from 25 to 2,000 seconds. At the end of each oxidation cycle, the chamber was evacuated to 1×10^{-8} torr, the beam-line gate valve was opened, and the thickness of the oxide film was measured by PEX.

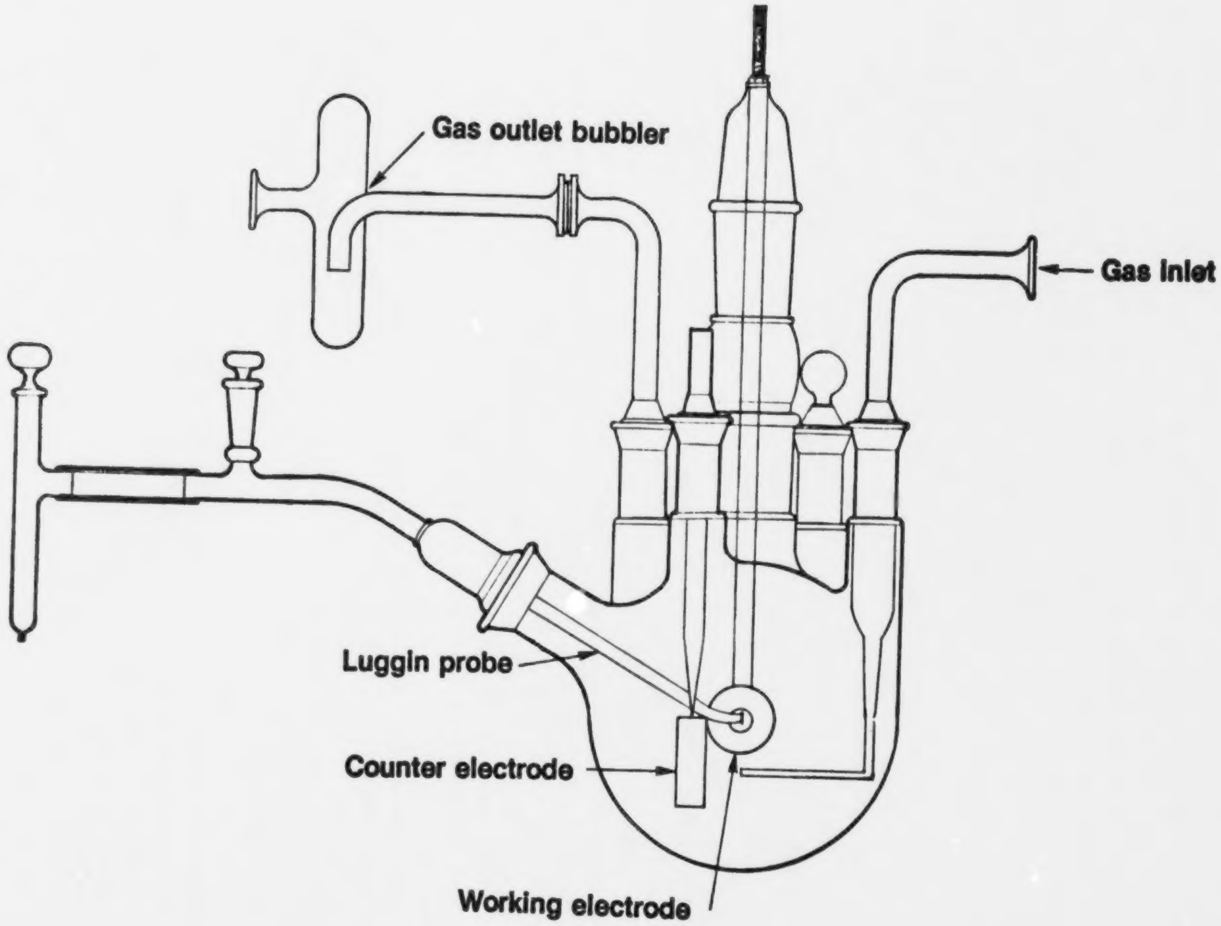


Figure 3. - Schematic of the electrochemical cell used to determine the anodic polarization behavior of the surface and bulk alloys.

Physical Properties Studies

Since the technique of forming surface alloys by ion implantation is considerably different from standard alloy fabrication techniques, an understanding of the physical metallurgy of surface alloy systems and, specifically, the determination of the alloy concentration as a function of depth (depth profile) is required in order to interpret their behavior in hostile environments. The theoretical depth profile calculated from the theory of Lindhard, Scharff and Schiott (designated LSS theory) for low-energy ions implanted into an amorphous material was shown in figure 1. Since this theoretical description had not been substantiated experimentally for metallic systems, it was important that experimental profiles be obtained for the surface alloys.

Figure 4 shows the depth profile of 25-keV nickel ions implanted into polycrystalline iron as determined experimentally using a combination of PEX and low-energy argon ion sputtering (5). A comparison of the experimental profile with the Gaussian-shaped profile of figure 1 indicates that the distribution has been shifted toward the surface and that the surface concentration is much higher than what would be expected. This phenomenon was explained by considering the effects of sputtering of the iron substrate during the implantation process on the final depth profile. This sputtering results in an erosion of the iron surface with removeal not only of iron atoms but also of previously implanted nickel atoms. Using an iterative procedure (5), the LSS throretical profile was modified to include the effects of sputtering, and the results are compared to the experimental profile in figure 4. The agreement is quite good, with the maximum in both profiles occurring at a final iron sample depth of 36 Å. The difference in the amplitudes of the distribution is believed to be due to the total uncertainty involved in the PEX profiling technique.

Figure 5 shows the experimentally determined profile for 25-keV chromium ions implanted into polycrystalline iron. The theoretical profile, modified to include the effects of sputtering, is also shown. The agreement is not as good as for the Fe-Ni surface alloys, but the effect of increasing the surface concentration caused by the sputtering is still observed.

To determine the effects of heat treatment on the nickel distribution in the Fe-Ni surface alloys, three surface alloys were heated to 500° C for 40 minutes, and the depth profiles of the nickel were subsequently obtained after cooling to room temperature. The results are shown in figure 6, with the theoretical annealed profile predicted by Fick's laws of diffusion (6) also shown. The heat treatment has caused the distribution of nickel to broaden more than what was expected by normal laws of diffusion and also resulted in a shift of the maximum of the distribution.

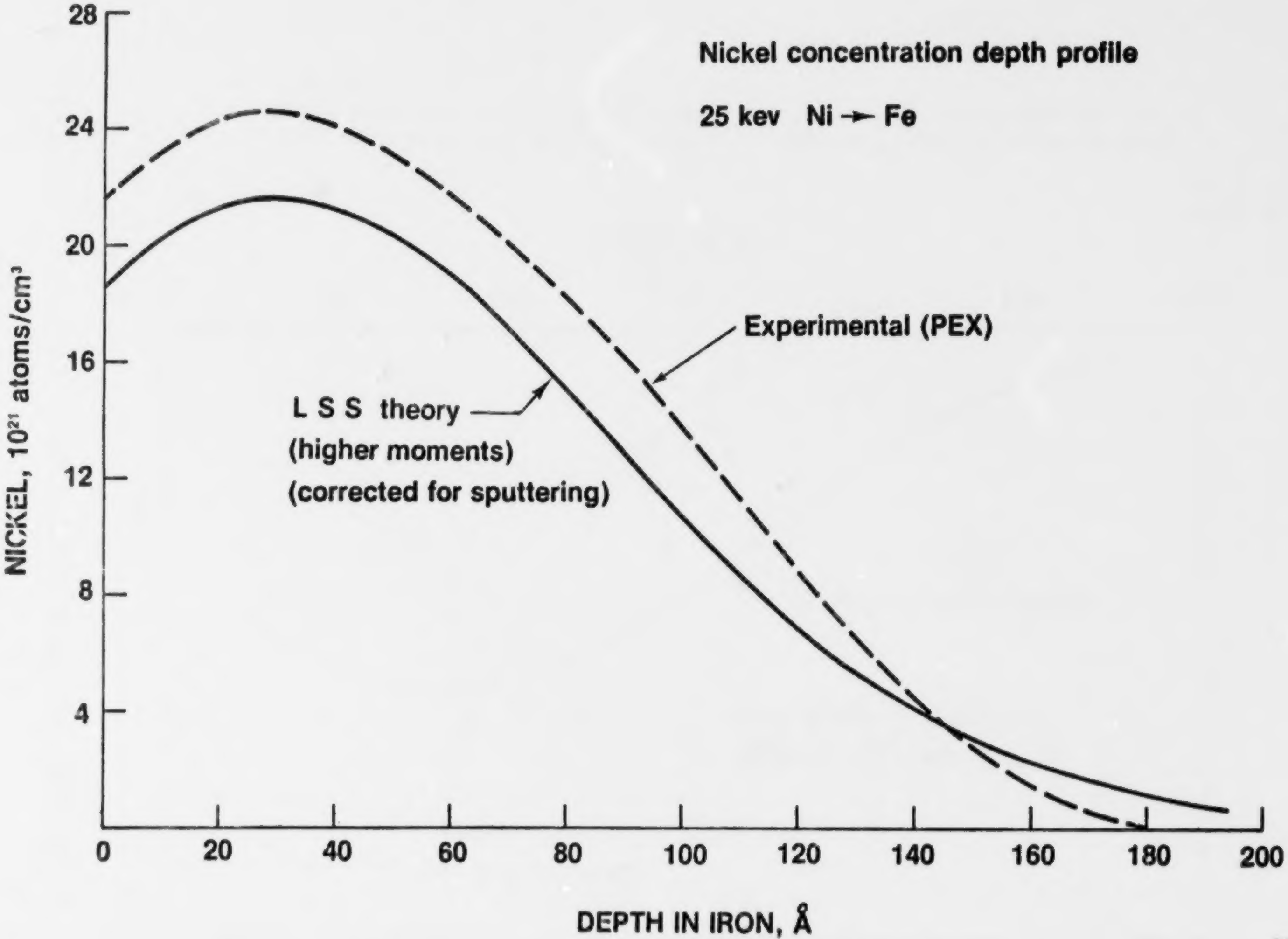
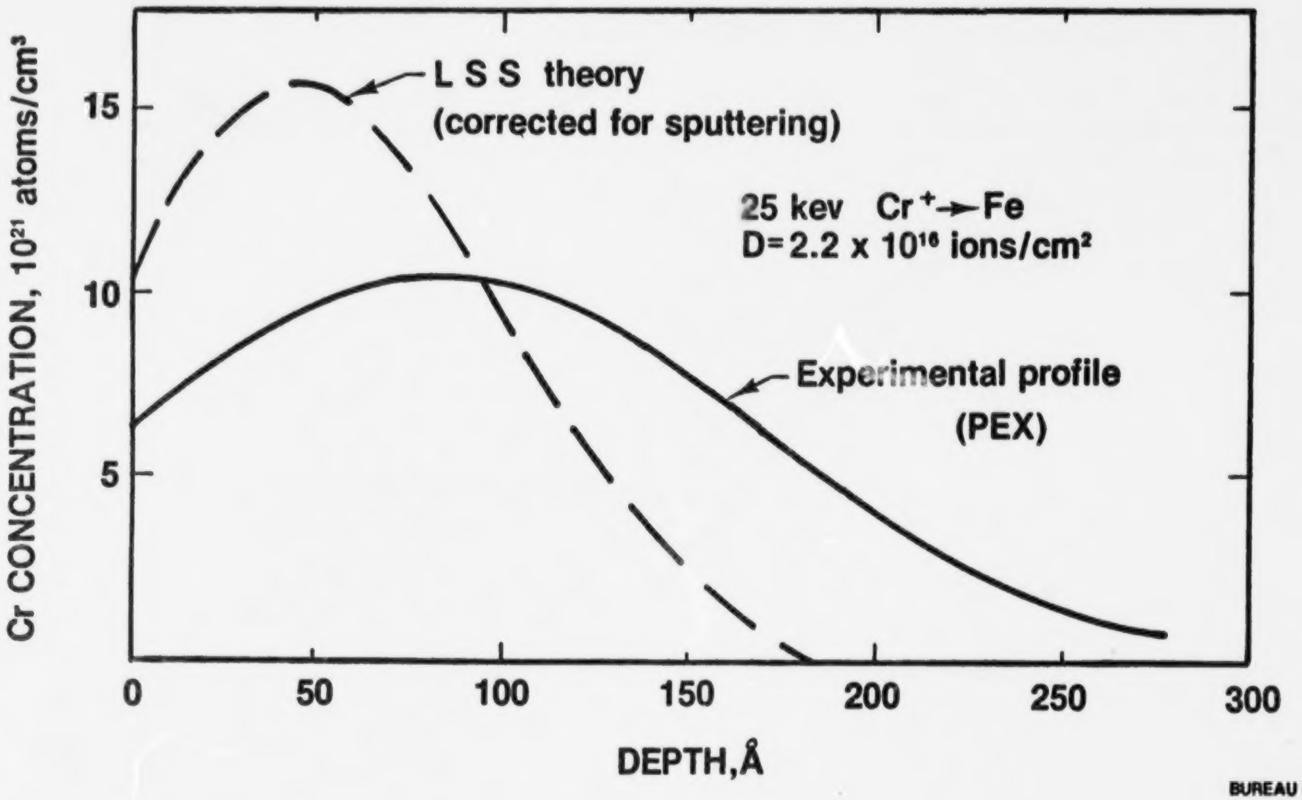


Figure 4. - Nickel depth profiles as determined experimentally and calculated from LSS theory modified to include sputtering of the metal substrate during implantation.

BUREAU OF MINES
H 10,898 CP



BUREAU OF MINES
H 10,740 CP

Figure 5. - Chromium depth profiles as determined experimentally and calculated from LSS theory modified to include sputtering of the metal substrate during implantation.

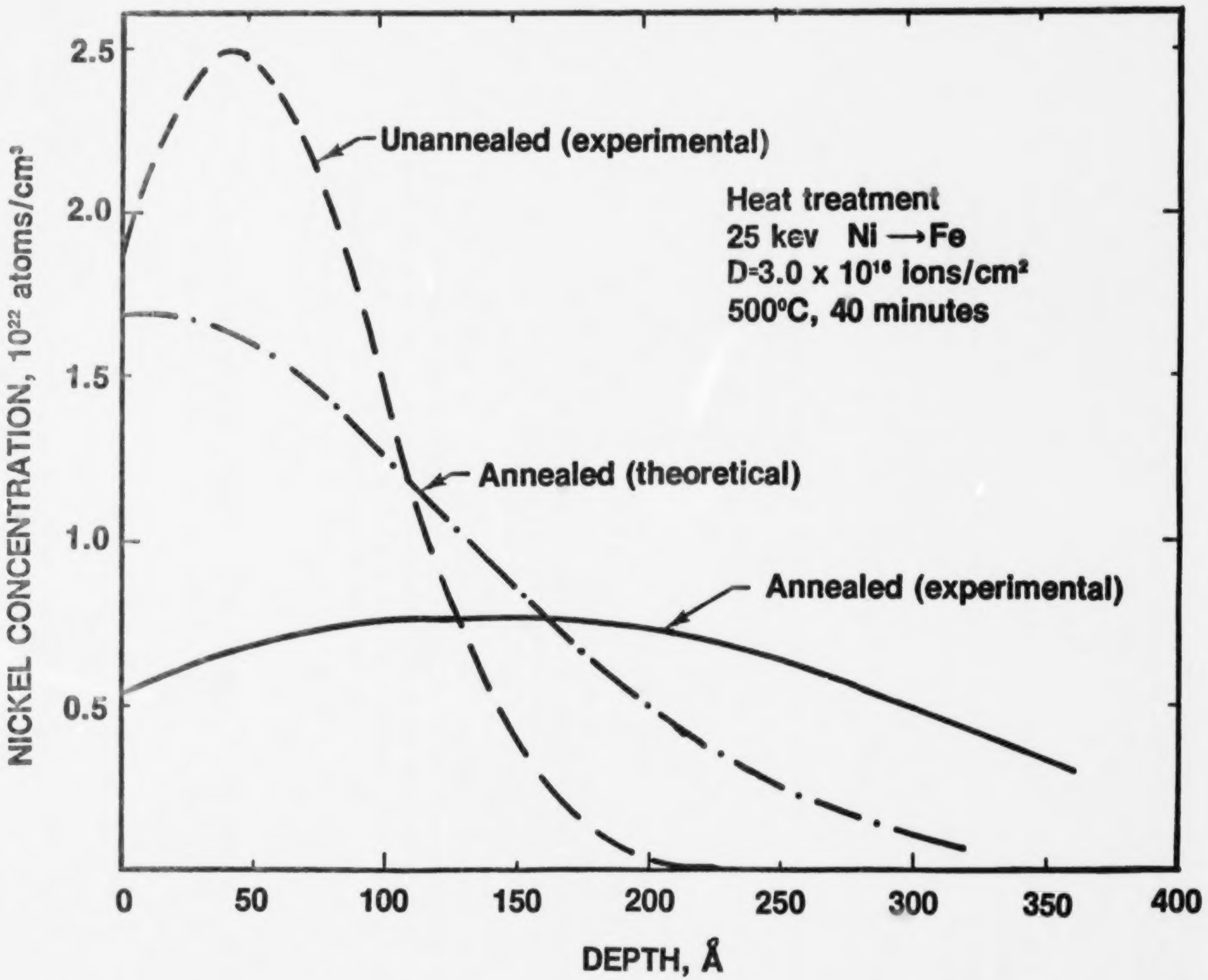


Figure 6. - Experimental depth profiles for an Fe-Ni surface alloy before and after heat treatment and a comparison to post-heat-treatment depth profile calculated from the unannealed depth profile using Fick's laws of diffusion.

BUREAU OF MINES
H 10,701 CP

Anodic Polarization Studies

This section reports the results of the studies conducted in order to determine the corrosion resistance of several binary surface alloys. The technique, chosen from the many chemical and electrochemical techniques available, was to make an electrochemical determination of the critical corrosion current, i_c, of the metal and the characteristic pitting potential, E_p, of the passive film. These two parameters are a relative indication of the general-corrosion resistance and pitting-corrosion resistance, respectively, and can be compared to the same parameters determined for equivalent commercial bulk alloys of known corrosion resistance. A decrease in the i_c and/or a shift of the E_p in the noble direction for the surface alloys is interpreted as indicating an improved overall corrosion resistance. A discussion of the validity of using this technique to determine i_c and E_p can be found in reference 2.

To demonstrate how the parameters i_c and E_p are determined, figure 7 shows the effect of several concentrations of Cl^- added to the buffered boric acid solution on the anodic polarization of pure iron. The Cl^-, added as NaCl, affected i_c, E_p, and the passive-region current density. The term i_c is equivalent to the commonly used term "critical current density" and is used here due to lack of a specific passivating potential for many of the alloys tested. The E_p is equivalent to the potential at which passivity breaks down. The electrochemical behavior of pure iron exposed to a pure buffered boric acid solution was characterized by an increase in current density that occurred as the potential was made more anodic than -520 mV vs. NHE (normal hydrogen electrode), also referred to as E_o, the crossover potential between the cathodic and anodic current regions. The current density peaked at a value of 1.4×10^{-5} amp/cm^2, representing i_c, at -400 mV. This was also the potential at which the active-passive transition occurred, causing a subsequent decrease in the current density. The passive current density remained constant at 1.2×10^{-6} amp/cm^2, and the E_p occurred at 1150 mV. Table 1 shows that the effects of Cl^- concentration on the corrosion current and E_p of iron are quite complex and that the effect of Cl^- on i_c is not as significant as its effect on the passive current densities (as shown by the onset of the E_p).

Table 1. - Effect of Cl^- concentration on electrochemical parameters of iron in a borate-buffered pH 8.5 solution

Cl^-, ppm	i_c, amp/cm	E_p, mV
0	1.4×10^{-5}	1150
10	3.8×10^{-5}	800
2400	4.5×10^{-5}	-140

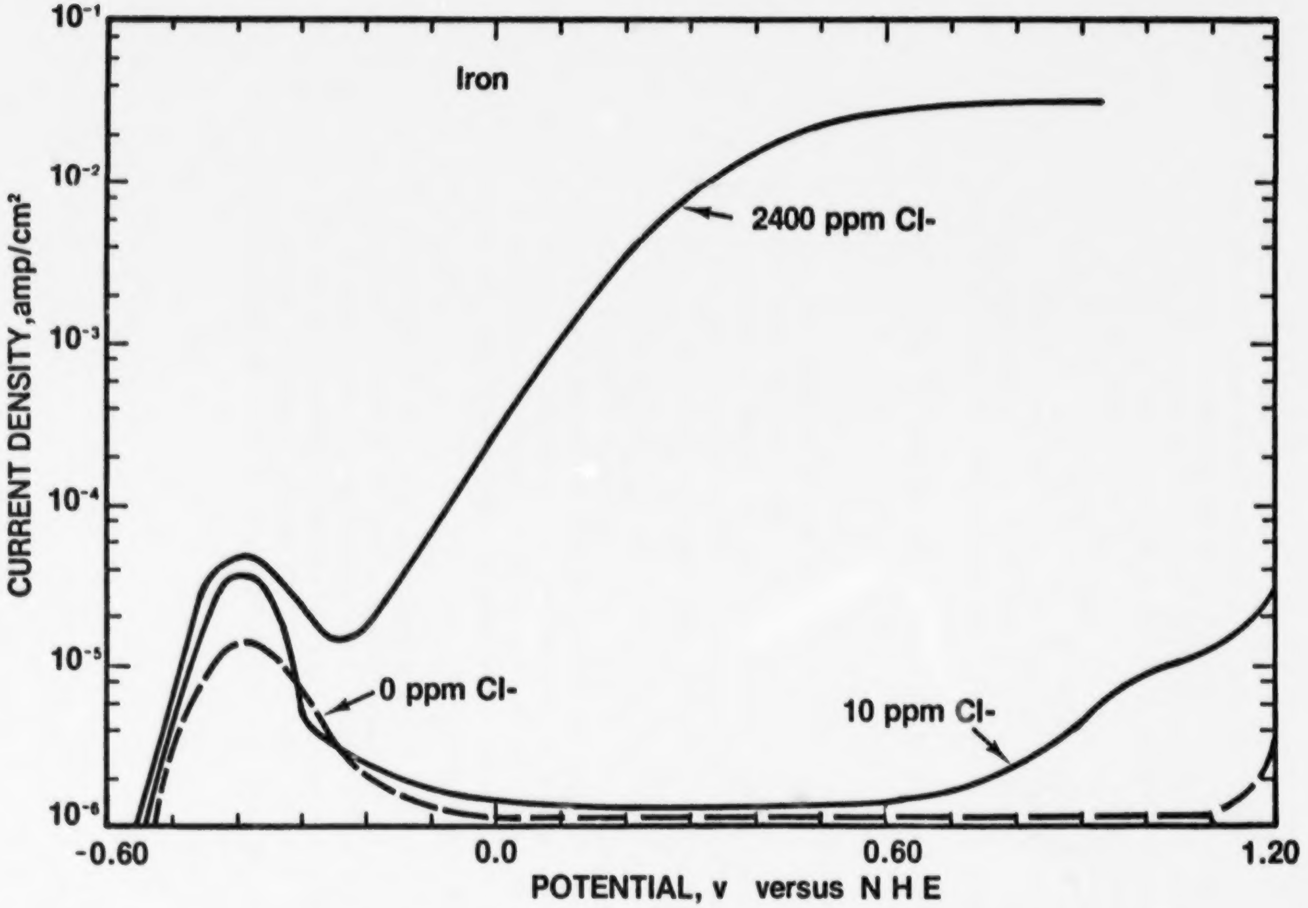


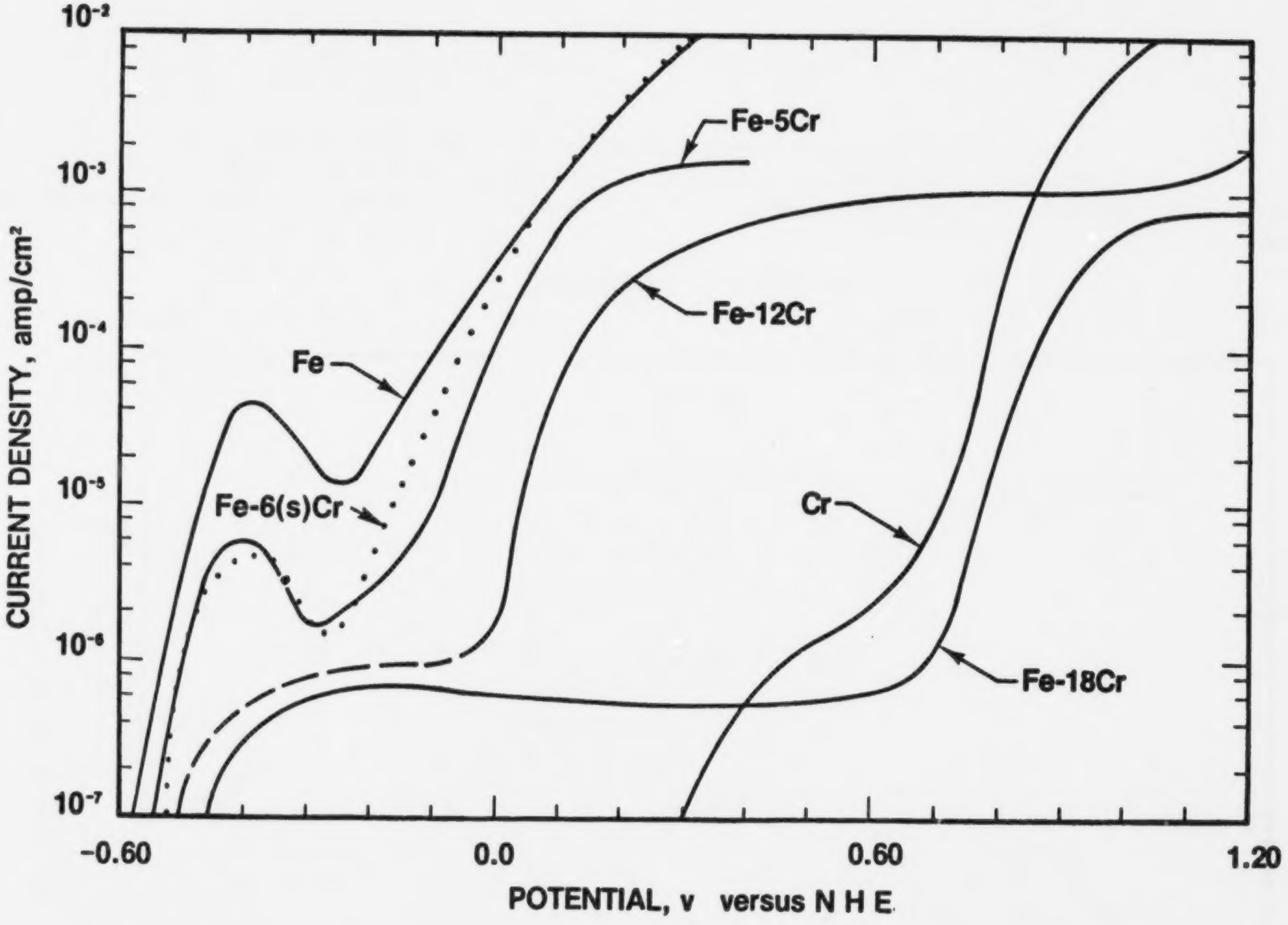
Figure 7. - Anodic polarization behavior (in a borate-buffered pH 8.5 solution) of iron showing the effect of chloride ion concentration on the electrochemical parameters.

BUREAU OF MINES
H 18,772 CP

Figures 8 and 9 compare the anodic polarization curves obtained for Fe-6(s)Cr and Fe-19(s)Cr, respectively, to those obtained from iron, chromium, and three Fe-Cr bulk alloys. With respect to the bulk alloys, the addition of chromium to iron results in (1) a reduction in i_c, (2) a shift of the crossover potential, E_o, towards the noble direction, and (3) a shift of E_p towards the noble direction. It can be seen from the figures that the same general effects are also obtained for the surface alloys. The addition of chromium by ion implantation (1) decreases i_c, resulting in a cathodic current for the Fe-19(s)Cr alloy in the region where anodic dissoluton is expected, and (2) causes the E_p to be more noble. Two effects that differentiated the behavior of the surface alloys from that of the bulk alloys were the elimination of the passive region for the Fe-19(s)Cr alloys and the location of the pitting potentials for surface and bulk alloys. The reason that the surface alloys do not exhibit an E_p as noble as their equivalent bulk alloy is probably the extreme thinness of the alloyed layer (250 Å).

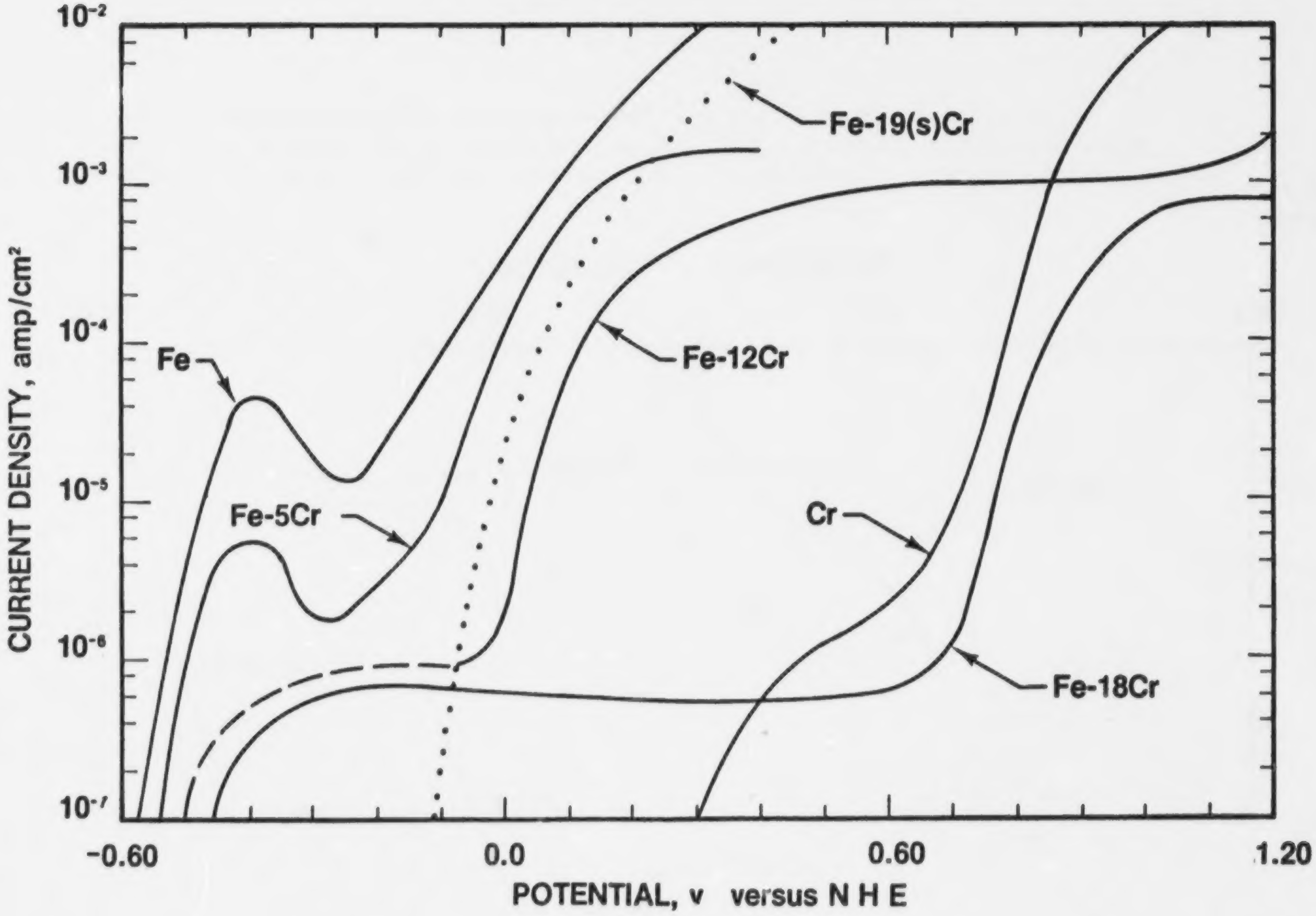
Figure 10 shows anodic polarization results for an Fe-25(s)Ni alloy compared with those for iron, nickel, and two commercially available steels. The bulk alloys tested were Type-9 nickel steel, a cryogenic steel containing nominally 9 wt-pct nickel, and Vascomax 250 (V-250), a high-strength maraging steel containing 18 wt-pct nickel and significant amounts of Co, Mo, Ti, Si, and Mn. The electrochemical behavior of the Fe-Ni bulk alloys shows effects similar to those obtained for the Fe-Cr bulk and surface alloys; however, the interpretation of the behavior of the V-250 may be somewhat speculative since the effects of the secondary elements (Co, Mo, Ti, etc.) have yet to be determined. By comparing the E_p's of the two steels, it can be stated that the V-250 has greater resistance to pitting than the Type 9 nickel steel. The polarization curve for the Fe-25(s)Ni alloy indicates that implantation of the nickel resulted in a significant reduction in i_c and caused the E_p to shift from -140 mV for iron to +80 mV for the Fe-25(s)Ni. This shift represents a substantial improvement in the resistance to pitting corrosion.

The pitting potentials of the surface and bulk alloys are summarized in table 2 in the order of increasing resistance to pitting corrosion. In general, all of the Fe-Cr bulk alloys exhibited electrochemical behavior that indicated better pitting corrosion resistance than any of the Fe-Cr surface alloys. The Fe-25(s)Ni alloy, however, had a greater resistance to pitting corrosion than all of the Fe-Ni commercial alloys tested.



BUREAU OF MINES
H 16773 CP

Figure 8. - Anodic polarization behavior (in a borate-buffered pH 8.5 solution with 2400 ppm Cl^- addition) of Fe-6(s)Cr compared with behavior of polycrystalline iron, chromium, and three Fe-Cr bulk alloys.



BUREAU OF MINES
H 16,780 CP

Figure 9. - Anodic polarization behavior (in a borate-buffered pH 8.5 solution with 2400 ppm Cl^- addition) of Fe-19(s)Cr compared with behavior of polycrystalline iron, chromium, and three Fe-Cr bulk alloys.

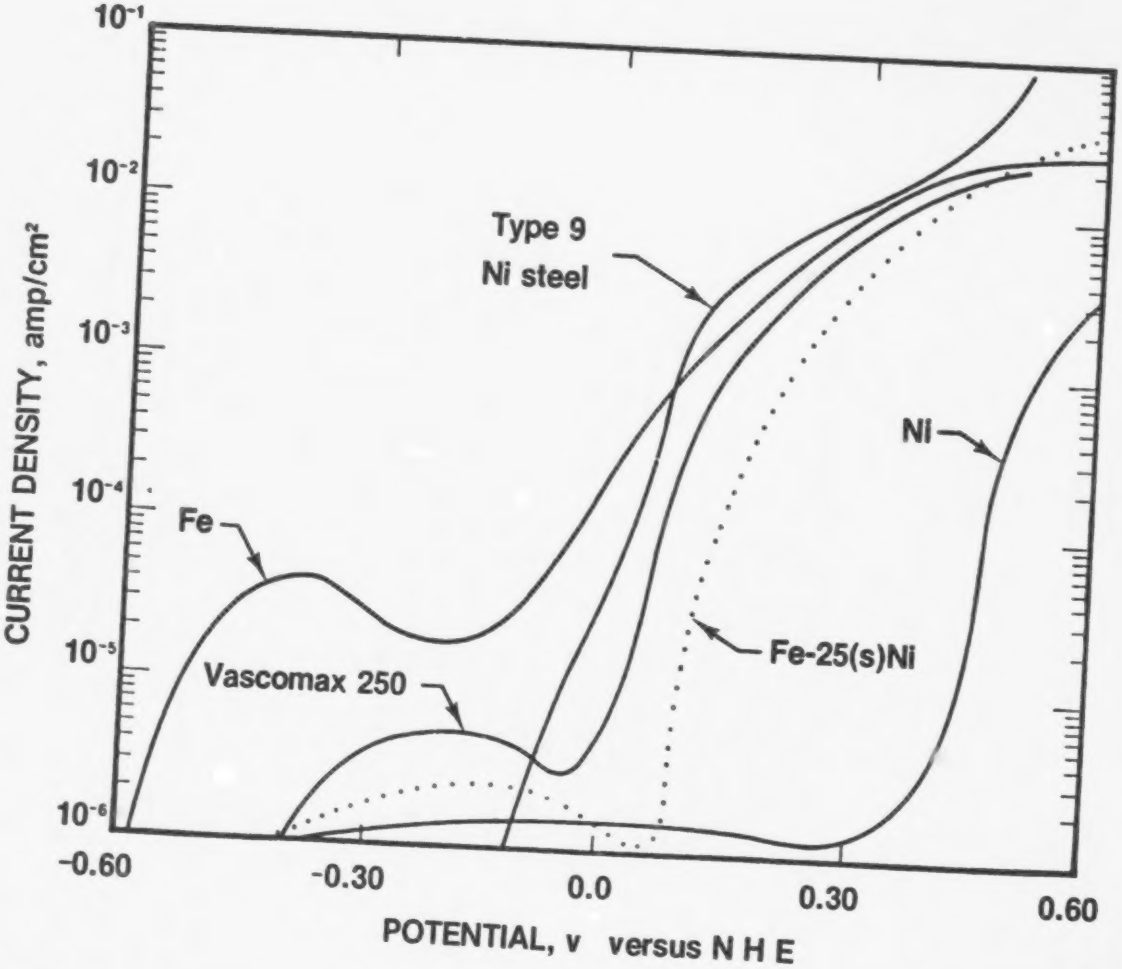


Figure 10. - Anodic polarization behavior (in a borate-buffered pH 8.5 solution with 2400 ppm Cl^- addition) of Fe-25(s)Ni compared with behavior of polycrystalline iron, nickel, and two commercial alloys.

BUREAU OF MINES
M 18,775 CP

Table 2. - Summary of pitting potentials for all alloys tested

Metal	E_p, mV
Fe-6(s)Cr	-260
Fe	-140
Fe-5%Cr	-140
Fe-19(s)Cr	-120
Type 9 Ni steel	-120
Fe-12%Cr	-20
V-250	5
Fe-25(s)Ni	80
Ni	410
Fe-18%Cr	680
Cr	700

Oxidation Studies

Metal loss for iron-based alloys through gaseous oxidation processes is a serious problem in most environments at temperatures greater than about 300° C. Unlike the problem of aqueous corrosion, where significant metal loss can occur at low (20° to 50° C) temperatures, oxidation in low-temperature, dry environments generally results in the formation of a thin oxide film that prevents further metal loss. At higher temperatures oxide films often separate from the metal substrate due to mechanical stresses at the film-metal interface, with subsequent significant metal loss due to the continuous reforming of oxide films.

In this study, the oxidation kinetics of Fe-22(s)Cr alloys were obtained at 300° C for an oxygen partial pressure of 4×10^{-6} torr with the oxide film thickness obtained as a function of exposure using PEX. For comparison, oxidation kinetics studies were carried out for Fe and an Fe-17.2 atomic percent Cr bulk alloy (designated Fe-17.2 Cr) under identical conditions. Prior to oxidation, the surface of each sample was sputtered with low-energy argon ions to remove any surface impurities.

Figure 11 shows the oxidation kinetics obtained for the Fe-Cr surface and bulk alloys for iron. Each data point is the average value for the oxidation of two samples. In calculating the oxide thickness from the oxygen concentration in atoms per square centimeter as determined by PEX, all of the oxides formed were assumed to be Fe_3O_4. This has been shown to be the case for iron (4). If the oxide films on either the bulk or surface alloys were completely Cr_2O_3 (worst case assumption), the error in oxide thickness would be 15 percent. The oxygen eposure in figure 11 is given in units of Langmuirs (10^{-6} torr-sec).

From figure 11 it can be seen that the surface and bulk alloys exhibit essentially identical oxidation results, whereas the rate of oxidation for the iron is considerably higher. The kinetics for iron are believed

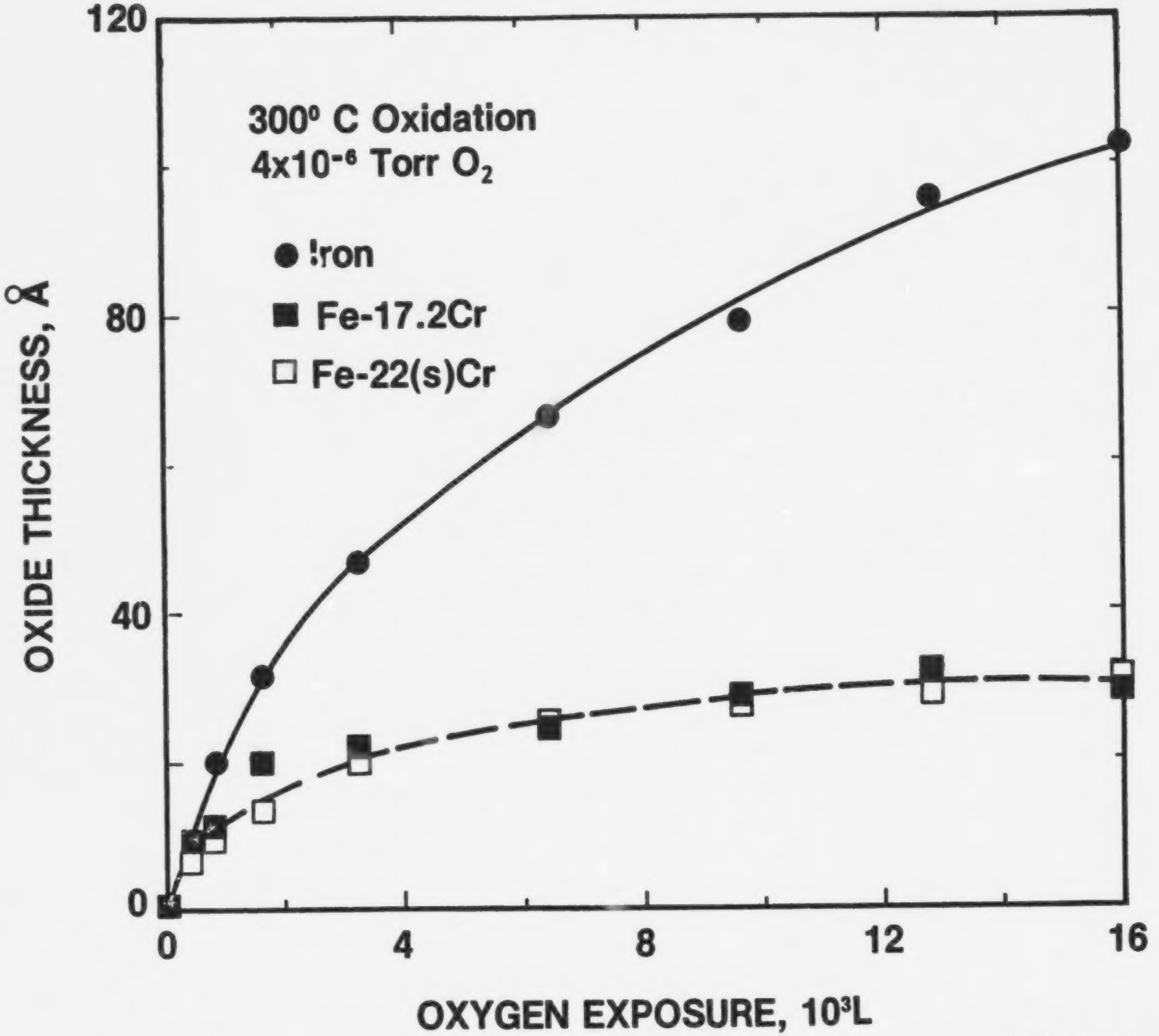


Figure 11. - Oxide thickness as a function of oxygen exposure for iron, Fe-17.2Cr bulk alloys, and Fe-22(s)Cr surface alloys oxidized at 300° C and 4 x 10^{-6} torr oxygen.

BUREAU OF MINES
H 10,506 CP

to represent an oxidation process where the rate of oxidation is limited by the diffusion of iron ions or vacancies, whereas for the surface and bulk alloys, the rate of oxidation is believed to be controlled by an electronic transport mechanism.

The use of iron-chromium surface alloys at 300° C is an ideal application for surface alloying. Very small quantities of chromium are needed to form the oxide films for oxidation protection since only small quantities of chromium are needed to change the electronic properties of the metal-oxide interface.

Summary and Conclusions

Surface alloys have been fabricated by the implantation of low-energy chromium or nickel ions into iron or commercial steel substrates. Composition profiles of the alloy concentration as a function of depth below the metal surface have been obtained for Fe-Cr and Fe-Ni surface alloys. The profiles were found to be of a Gaussian-distribution character, agreeing reasonably well with profiles calculated using LSS theory, provided that sputtering of the metal substrate during implantation was taken into account.

The effect of heat treatment at 500° C on the alloy distribution has been studied for the Fe-Ni surface alloys. The redistribuiton of the implanted nickel generally followed Fick's law; however, a shift in the maximum of the concentration profile away from the surface was observed. This observation implies diffusion against a concentration gradient, and the mechanism for this may involve radiation-enhanced diffusion.

The aqueous and gaseous corrosion characteristics of the surface alloys have been studied using anodic polarization techniques and oxidation at 300° C, respectively. The results have shown that (1) in terms of reducing gaseous oxidation and general corrosion, Fe-Cr surface alloys are comparable to bulk Fe-Cr alloys, and (2) in terms of reducing pitting corrosion, Fe-Ni surface alloys are comparable to bulk Fe-Ni alloys.

In considering whether surface alloying by ion implantation can potentially replace certain bulk-alloying or electroplating techniques, the advantages and disadvantages should be considered. The principal advantage of surface alloying is that enormous reductions in the consumption of domestically scarce alloying elements would be realized. In this report, the resistance of surface and bulk alloys to general corrosion in an aqueous environment and to gaseous oxidation has been shown to be essentailly equivalent. The amount of the alloying element consumed in fabricating the surface alloy samples for these studies ranged from six to seven orders of magnitude less than the amount present in the bulk alloy sample.

A second advantage is that the implanted elements become an integral part of the base metal substrate. Surface alloying, therefore, would be superior to other types of surface protection techniques such as the application of coatings, since there would be no interfacial weakness and no adherence problems, and the number of atoms implanted and their distribution as a function of depth could be accurately controlled.

A third advantage is that alloys can be fabricated by ion implantation that cannot be formed using conventional alloying techniques. Since ions are forcibly implanted into the base metal, normal solid-solubility limits can be exceeded. New alloy systems not available by present state-of-the-art techniques can, therefore, be formed and studied by ion implantation.

A possible fourth advantage exists in a comparison with conventional electroplating techniques, which are known to produce toxic wastes that contribute to both air and water pollution. Clean air and water standards are now restricting or eliminatng the use of electrolytic coatings as an alternative to bulk alloying. Ion implantation, on the other hand, produces no byproducts that contribute to air or water pollution.

One of the principal disadvantages of surface alloying by ion implantation is that it is a "line-of- sight" process. Only surfaces that are directly exposed to the incident ion beam can be alloyed. Another disadvantage is that there is a limited depth to which the ions can be implanted. In general, approximately 500 nm will be the maximum implantation depth attainable, and the use of surface alloys may be limited in abrasive environments. It should be pointed out, however, that many bulk stainless steels can only be used in abrasion-free environments because of susceptibility to pitting corrosion if the protective oxide film is abraded away. A third disadvantage is that the surface alloys must be fabricated in a vacuum environment. This may be a limiting factor in using the surface-alloying technique for certain types of metal structures.

References

1. G. Dearnaley, J. H. Freeman, R. S. Nelson, and J. Stephen. Ion Implantation. North-Holland, Amsterdam, The Netherlands, 1973.

2. P. B. Needham, Jr., B. D. Sartwell, and B. S. Covino, Jr., Anodic Polarization Behavior of Fe-Cr Surface Alloys Formed by Ion Implantation. J. Electrochem. Soc., (to be published).

3. N. D. Greene. Experimental Electrode Kinetics. Rensselaer Polytechnic Institute, Troy, New York, 1965.

4. P. B. Needham, Jr., H. W. Leavenworth, and T. J. Driscoll. The Kinetics of Thin Oxide Film Formation on Iron Using Proton-Impact-Excited X-ray Analysis. J. Electrochem. Soc., 120, 1973, pp. 778-783.

5. B. D. Sartwell, A. B. Campbell, and P. B. Needham, Jr. Formation of Corrosion-Resistant Surface Alloys by Implantation of Low-Energy Nickel and Chromium Ions Into Polycrystalline Iron. Ch. in Ion Implantation in Semiconductiors and Other Materials, ed. by F. Chernow, Plenum, New York, 1977, pp. 201-12.

6. J. Crank. The Mathematics of Diffusion. University Press, New York, 1957.

Surface Alloying by Ion Implantation: An Alternative to Cadmium Electroplating

DISCUSSION PERIOD

MR. DAGE: Have you done any studies comparing this technique with these metals to the use of cadmium or cadmium-plating.

MR. SARTWELL: No, we haven't. That is something we would like to get involved in, but we haven't made any direct comparisons to cadmium electroplated steel.

Alternative Materials and Processes

Session I

Tuesday Morning 12:10

ION VAPOR DEPOSITED ALUMINUM COATINGS

E. R. Fannin
McDonnell Aircraft Company
St. Louis, Missouri 63166

A process for the application of dense, uniform, and very adherent aluminum coatings has achieved production status. The process is a vacuum coating process and is referred to as ion vapor deposition (IVD). It can be used to replace cadmium coatings almost exclusively. Aluminum coatings can be used at temperatures up to 925°F, whereas cadmium is limited to 450°F. The IVD process can be used to coat high strength steel without fear of hydrogen embrittlement. It can also be used in contact with titanium without causing solid metal embrittlement. Cadmium is prohibited for this application. Finally, ion vapor deposition is a clean process and does not contribute to any ecology problems.

Details of the ion vapor deposition process, performance data, and current production applications at McDonnell Aircraft Company on both Navy and Air Force Programs will be discussed.

Preceding page blank

ION VAPOR DEPOSITED ALUMINUM COATINGS

by

E.R. Fannin
McDonnell Aircraft Company
Dept 247, Bldg 32
P.O. Box 516
St. Louis, Missouri 63166

Abstract

A process for the application of dense, uniform, and very adherent aluminum coatings has achieved production status and can be used to replace cadmium almost exclusively. The process is a vacuum metallizing process and is referred to as ion vapor deposition. Aluminum coatings can be used at temperatures up to 925°F (496°C), whereas cadmium is limited to 450°F (232°C). The process can be used to coat high strength steel without fear of hydrogen embrittlement. It can also be used in contact with titanium without causing solid metal embrittlement. Cadmium is prohibited for this application. Finally, ion vapor deposition is a clean process and does not contribute to any ecology problems.

Details of the ion vapor deposition process, performance data, and current production applications at McDonnell Aircraft Company on both Navy and Air Force Programs will be discussed.

Introduction

Cadmium electroplating was the favored method for protecting steel on aircraft structure for many years. Obvious problems with its use were minimal prior to the use of high strength aluminum and steel alloys. Cadmium plated fasteners installed in high strength aluminum alloys helped promote exfoliation corrosion in the countersinks and hydrogen embrittlement often occurred when electroplating cadmium on high strength steel. More recently it has received further disfavor because it was found to cause solid metal embrittlement of titanium structure and because of its toxicity and harmful effects on the environment.

However, it was mainly for the first two reasons that we at McDonnell Aircraft Company (a division of McDonnell Douglas Corporation) started looking for a viable alternate for cadmium in the early 1960's. After extensive paper studies, aluminum coatings were selected as the best substitute. Being the least dissimilar to aluminum alloy structure, it is ideally compatible. Furthermore, aluminum is anodic to steel and provides galvanic protection as does cadmium.

It was quickly found that available processes for applying aluminum coatings such as metal spraying, electroplating, cladding, hot dipping and others had severe limitations such as thickness control, adhesion, size and shape of product that could be coated, and effect on substrate properties.

During this same period we had selected vacuum deposited cadmium as the coating for solving the problem of hydrogen embrittlement of high strength steel. Our production experience with the vacuum cadmium coating process was very favorable. For this reason we started looking at vacuum coating processes for aluminum. This included physical vapor deposition, ion vapor deposition, and chemical vapor deposition. Ion vapor deposition provided the best adhesion and most uniform coating thickness and with other considerations was selected for further development.

The performance advantages of ion vapor deposited (IVD) aluminum have since been confirmed in both laboratory and service tests and the process has reached production status. This high performance protective coating is also environmentally clean. The following is therefore a description of the process, the equipment, the coating performance, and illustrations of typical applications.

Discussion

Description of the Equipment and the Process

The basic equipment required for ion vapor deposition, called Ivadizer^R at McDonnell, is a steel chamber, a pumping system, an evaporation source, and a high voltage power supply. A schematic of a typical IVD unit is shown in Figure 1.

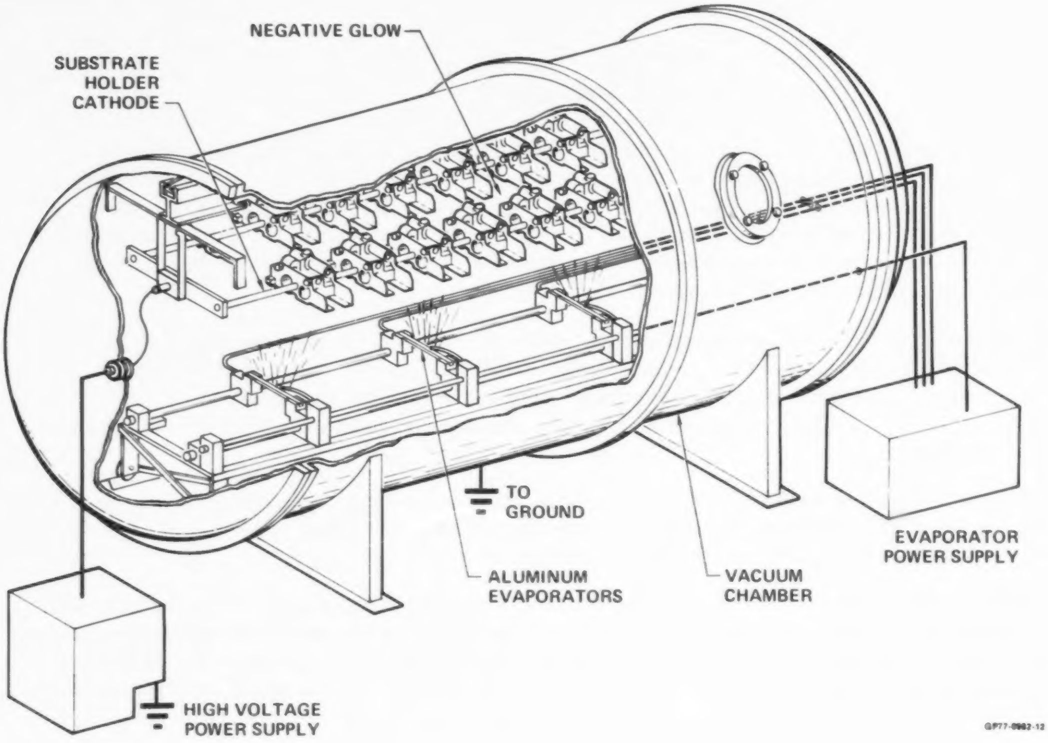


FIGURE 1
SCHEMATIC OF AN ION VAPOR DEPOSITION SYSTEM

The process sequence consists of pumping the system down to about 10^{-4} Torr. The chamber is then backfilled with an inert gas to about 10 microns and a high negative potential applied between the parts being coated and the evaporation source. The gas becomes ionized and creates a glow discharge around the parts to be coated. The positively charged gas ions bombard the surface of the parts and perform final cleaning. The clean surfaces resulting are essential for good coating adhesion.

Following glow discharge cleaning, commercially available aluminum wire (1100 alloy) is evaporated by continuously feeding into resistance heated crucibles. As the aluminum vapor passes through the glow discharge, a portion of it becomes ionized. This, in addition to bombardment by the inert gas ions, accelerates the aluminum vapor toward the part surface. This results in denser coatings and also improves the coating adhesion. The ionization also provides better throwing power and allows complex shapes to be more uniformly plated.

A typical plating cycle for coating detail parts would consist of the following:

1. Pump down to 10^{-4} Torr - 15 minutes
2. Backfill with inert gas - 2 minutes
3. Glow discharge clean - 15 minutes
4. Plate - 10 minutes
5. Backfill to atmosphere - 3 minutes

The total coating cycle requires about 45 minutes.

After coating, parts are generally chromate treated in accordance with MIL-C-5541 (Reference 1). This provides additional protection against corrosion. It also provides a good base for paint adhesion and is a common requirement for aluminum surfaces.

Technical Advantages

IVD aluminum coatings have several advantages over other coatings used to protect both steel and aluminum alloy parts. Advantages include:

1. Useful temperature to 925°F (496°C). Cadmium is limited to 450°F (232°C) (Reference 2 and 3).
2. Replace diffused nickel-cadmium and provide better corrosion protection at all strength levels. Diffused nickel-cadmium is limited to steels having strength levels below 200,000 psi because of hydrogen embrittlement and has a salt spray requirement of only 100 hours.
3. Does not cause solid metal embrittlement of titanium. Cadmium plating is prohibited.
4. Can be used in contact with fuel. Cadmium is prohibited.
5. Provides galvanic protection to aluminum alloys and does not cause fatigue reduction. Anodize coatings provide only barrier coating protection and cause fatigue reduction.
6. Can be applied thinner than alclad on aluminum alloys resulting in weight savings and is not limited to rolled forms.
7. Neither the process nor the coating create toxic materials and therefore do not present any ecology problems.

Coating Performance

An evaluation of 33 different coatings on fasteners was made by the Air Force and the Naval Air Development Center on service aircraft (Reference 4). IVD aluminum was rated as one of the top three coatings. The other two coatings were also metallic aluminum coatings that outperformed cadmium plated fasteners.

IVD aluminum is a soft, ductile coating and has properties nearly identical to pure aluminum. We use three classes and two types of coatings. The classes reflect coating thickness and the types are I, as coated, and II, as coated with a supplementary chromate treatment. Type II is generally used for reasons previously mentioned. The corrosion resistance requirement for type II coatings is shown in Table 1 for the various class coatings.

TABLE 1
MINIMUM CORROSION RESISTANCE REQUIREMENTS PER MIL-C-83488 (REFERENCE 2)

Class	Thickness (mils)	Corrosion Resistance (hrs)
1	0.0010 Minimum	672
2	0.0005 Minimum	504
3	0.0003 Minimum	336

Class 1 coatings are used for high temperature and exterior applications where severe corrosion environments are encountered. Class 2 is recommended for interior parts where less severe environments are encountered, and Class 3 is used only when close tolerances are required such as fine threaded parts.

Numerous corrosion tests have been performed on IVD aluminum coatings by McDonnell, the Air Force, the Navy, the Army, and by other companies. As usual with corrosion testing, there is a wide range of results. Some general conclusions can be drawn, however, using cadmium for comparison.

Corrosion testing of bright electroplated cadmium on steel panels along with IVD aluminum of comparable thickness in 5% salt spray per Federal Standard No. 115 will generally show cadmium to be better. However, if a scratch is made through the coatings to the substrates, the cadmium will generally sacrifice itself more quickly and allow red rust to form before the IVD aluminum.

Results obtained in laboratory tests when cadmium and IVD aluminum coated steel fasteners were installed in 7075-T6 aluminum alloy and exposed to SO_2 - salt spray for 168 hours are shown in Figure 2. The cadmium plated fastener heads are more severely rusted. More important is the condition of the countersinks in the aluminum. The IVD aluminum has provided protection to the countersinks while the cadmium coated fasteners appear to have promoted corrosion of the countersinks.

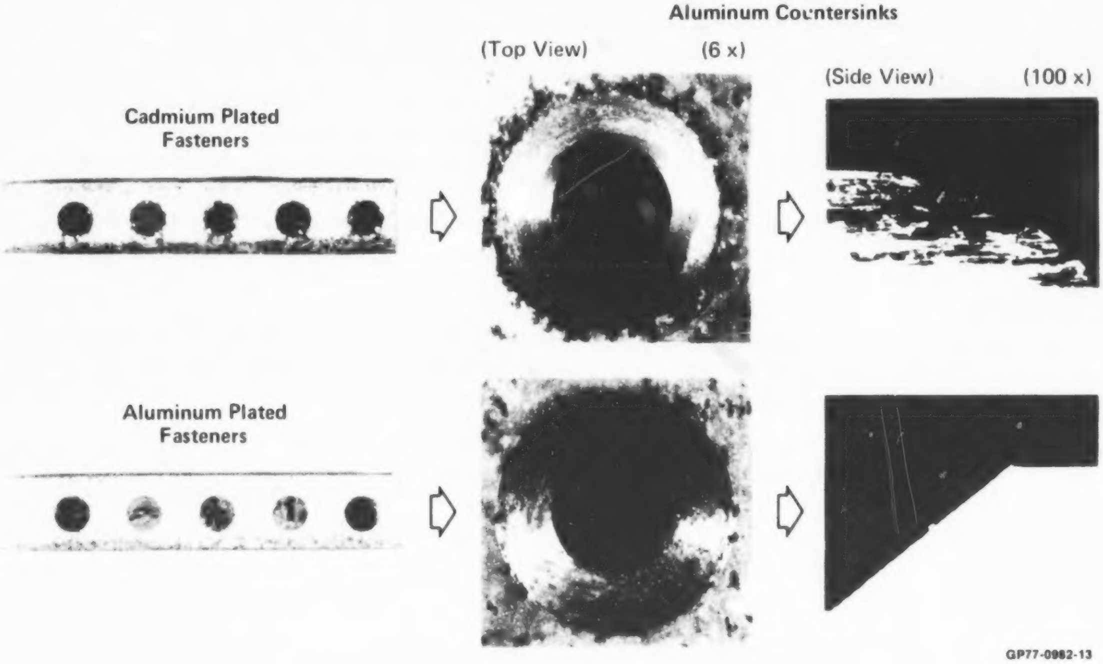
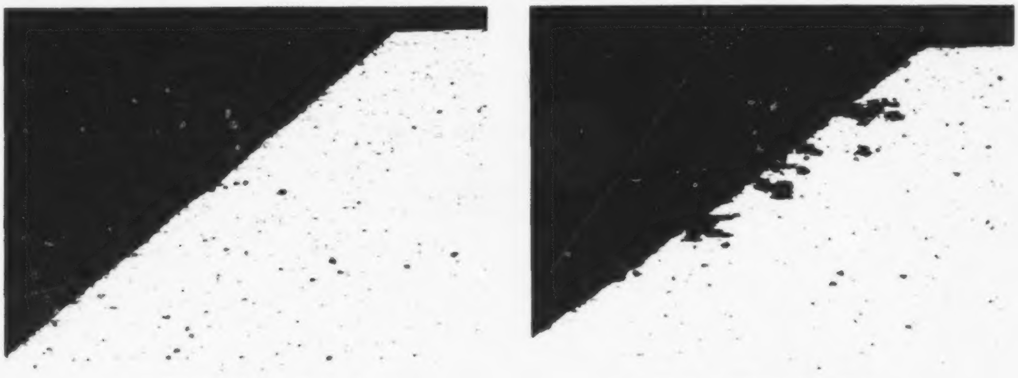


FIGURE 2
IVD ALUMINUM AND CADMIUM COATED STEEL FASTENERS INSTALLED IN 7075-T6 ALUMINUM ALLOY AND EXPOSED TO 168 HOURS OF SO_2 - SALT SPRAY

There are also advantages for IVD coating titanium fasteners installed in aluminum structure. A comparison was made between IVD aluminum coated titanium fasteners installed dry, and bare titanium fasteners installed with wet epoxy primer. The latter is a standard procedure used on aircraft. These fasteners were installed in 7075-T6 aluminum alloy that had been MIL-C-5541 treated. After fastener installation the panel was sprayed with one coat of MIL-C-23377 primer and exposed to SO_2 salt spray for 28 days. Visual examination showed that the blistering of primer around the peripheries of the fasteners installed with wet primer was more severe than around the IVD aluminum coated fasteners. Examination of the countersinks after fastener removal also showed less corrosion resulted where the IVD coated fasteners were installed (Figure 3). Studies at McDonnell have also shown a cost advantage of using IVD aluminum coated fasteners in lieu of wet installation.



IVD Aluminum Coated Fastener

Bare Titanium Fastener Wet Installed

FIGURE 3
CORROSION TESTS OF IVD COATED AND WET INSTALLED TITANIUM FASTENERS IN 7075-T6 ALUMINUM ALLOY COUNTERSINKS

Coating adhesion and thickness uniformity are comparable to electroplating. The adhesion requirements are the same as those specified in Reference 3 for cadmium electroplating. An example of the coating uniformity on a fastener is illustrated in Figure 4.

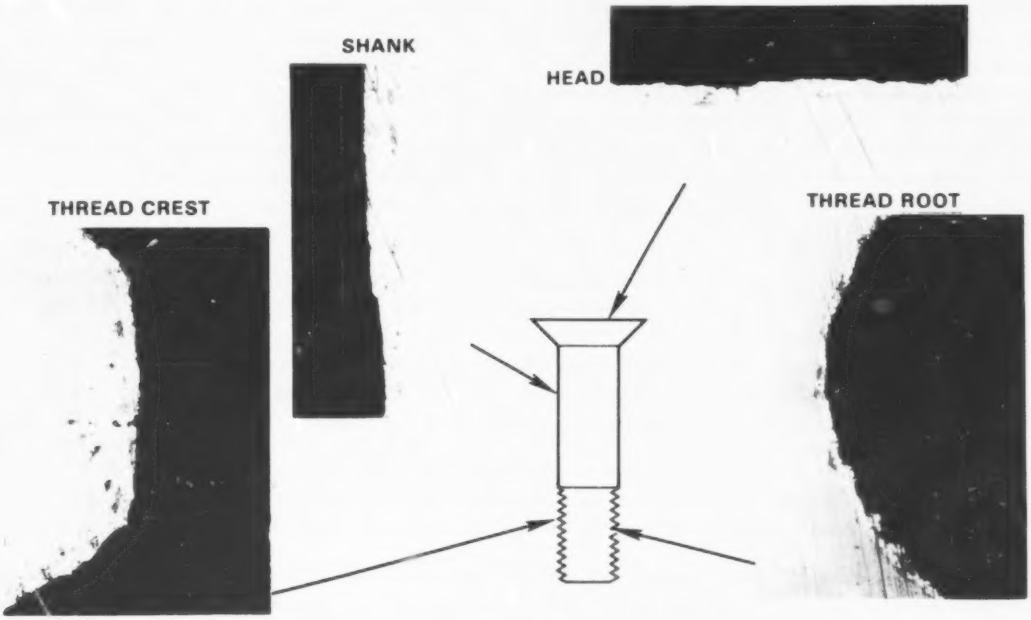


FIGURE 4
IVD ALUMINUM THICKNESS DISTRIBUTION ON A FASTENER

A lot of fastener qualification data has been generated on the use of IVD aluminum (Reference 5). A summary of the tests performed is listed in Table 2. This data is too voluminous to present here, however the conclusions can be summarized as follows:

1. IVD aluminum does not produce any detrimental effects on the mechanical properties.
2. The coefficient of friction of aluminum is higher than cadmium, therefore, higher installation forces are required. These higher values, however, are within the working ranges presently used for cadmium in most cases. Interference fit fasteners may require closer attention to the type of lubricants used.

TABLE 2
FASTENER QUALIFICATION TESTS

Mechanical	Installation
Tensile Strength	Torque Tension
Double Shear	Locking Torque
Tension Fatigue	Reuseability
Stress Durability	Interference Fit
Stress Rupture	

Production Status

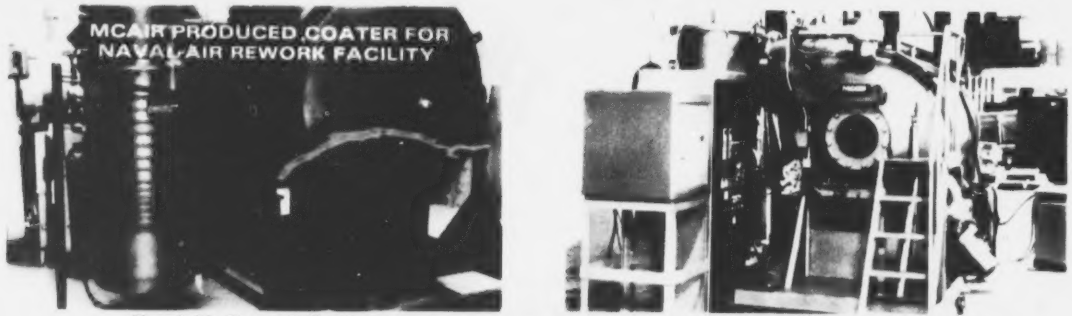
The first production size coater was sponsored by the Naval Air System Command and delivered to the Naval Air Rework Facility at North Island, San Diego, in April 1974. During this contract period a number of our aircraft parts, both steel and aluminum components, were plated and evaluated. Coating uniformity, adhesion and corrosion performance were all very satisfactory. This unit was 4 feet in diameter and 8 feet long and is shown in Figure 5.

At about this same time a new approach was conceived for coating small parts on a more economical basis. The technique is similar to barrel electroplating in that parts are placed in rotating barrels over the aluminum evaporation source. Following conceptual verification in the laboratory, a 4 foot diameter by 6 foot long system was designed and fabricated. The unit has been used to demonstrate the process and as a test bed for design development. The system has evolved from one barrel to two barrels per unit, doubling the output. Production capacity was increased further by placing vacuum locks on the feed and discharge ends of the system (Figure 6). This allows fasteners to be loaded and unloaded without breaking the vacuum and reduces the total coating cycle by about 50 percent. A similar unit installed this year at a fastener manufacturer, The Voi-Shan Corporation, is also shown in Figure 5.

Early in 1976 a large detail parts coater 7 feet in diameter and 12 feet long was installed in our manufacturing facility (Figure 5). Approval had been obtained from the Air Force to use ion vapor deposited aluminum coatings on the F-15 Eagle. Fatigue improvement and economics were the motivating reasons. Sulfuric acid anodize coatings were replaced on fatigue critical aluminum wing skins. This resulted in a fatigue improvement without a design configuration change. It also eliminated a shot peening operation, resulting in a cost savings. In addition, IVD coated low alloy steel was used to replace higher cost stainless steel components.

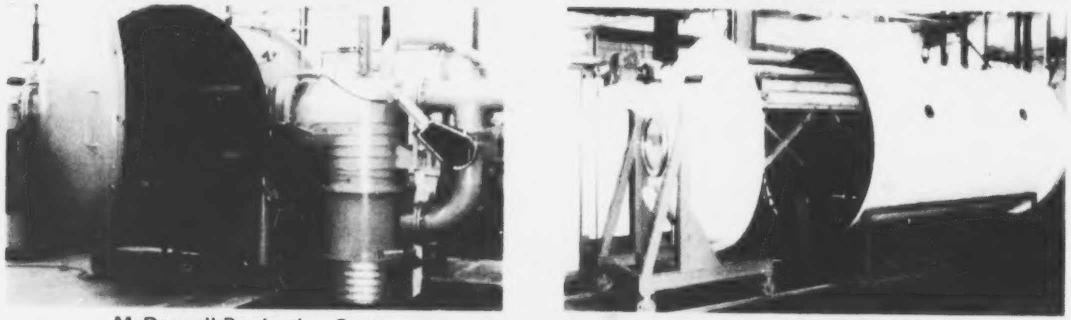
IVD aluminum is presently being used on the F-4 Aircraft and is required for use on the Harrier and the F-18 Hornet. It will be the primary corrosion protective plating on the F-18. On this aircraft it will be utilized on all fatigue critical aluminum structure, all high strength steel structure and on titanium and low alloy steel fasteners.

A unit has also been fabricated under contract with the Air Force Materials Laboratory, Manufacturing Technology Division. This unit is presently at McDonnell and is being used to develop optimum parameters and fixturing for coating both aircraft and engine parts. It will be utilized mainly as a replacement for vacuum deposited cadmium on high strength steel parts. This unit is 6 feet in diameter and 10 feet long (Figure 5).



Naval Air Rework Coater

Barrel Coater

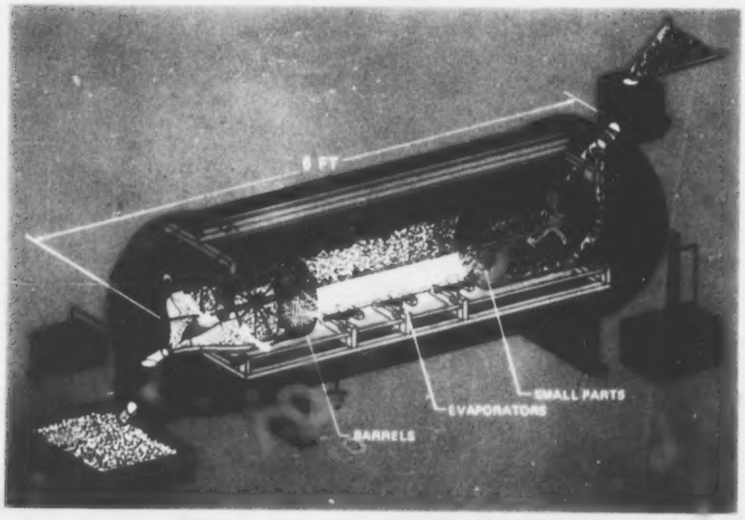


McDonnell Production Coater

Air Force Coater

GP77-0982-15

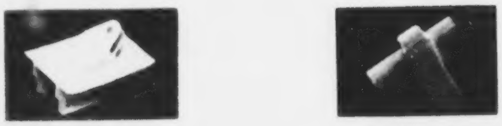
FIGURE 5
PRODUCTION COATERS



GP77-0982-16

FIGURE 6
SCHEMATIC OF BARREL COATER

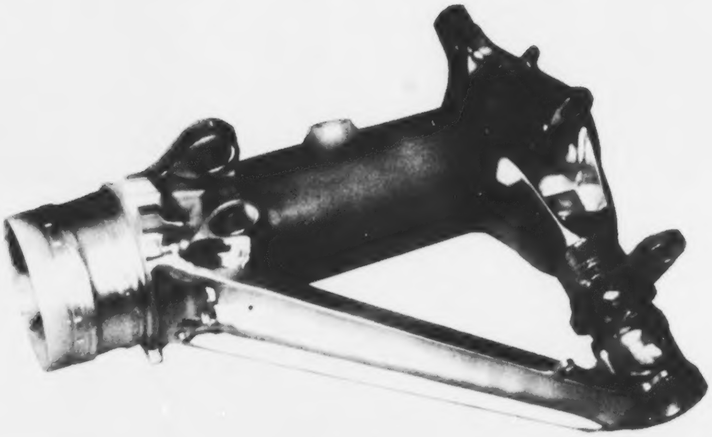
A photograph of a few of the aircraft and engine parts that have been coated at McDonnell are shown in Figure 7. There is also a lot of interest in aluminum coatings outside the aircraft industry. A few examples include computer discs, comsumer hardware, automotive parts, space systems, electrical components, appliances, etc. Examples of sample parts coated for evaluation are shown in Figure 8.



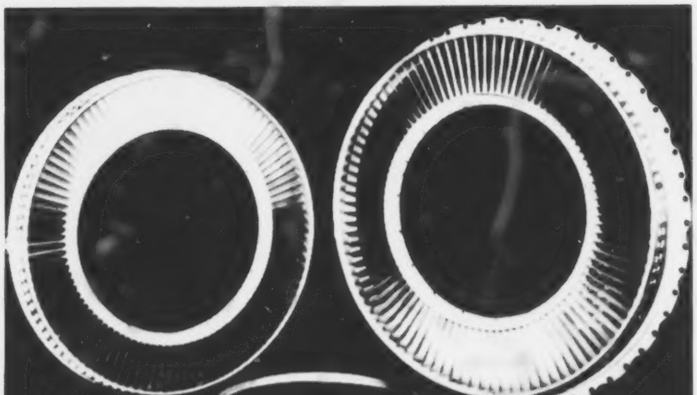
Engine Mount

Bellcrank

Wing Skin



Landing Gear



Stator Vane Assemblies

GP77-0882-17

FIGURE 7
IVD ALUMINUM COATED AIRCRAFT AND ENGINE PARTS

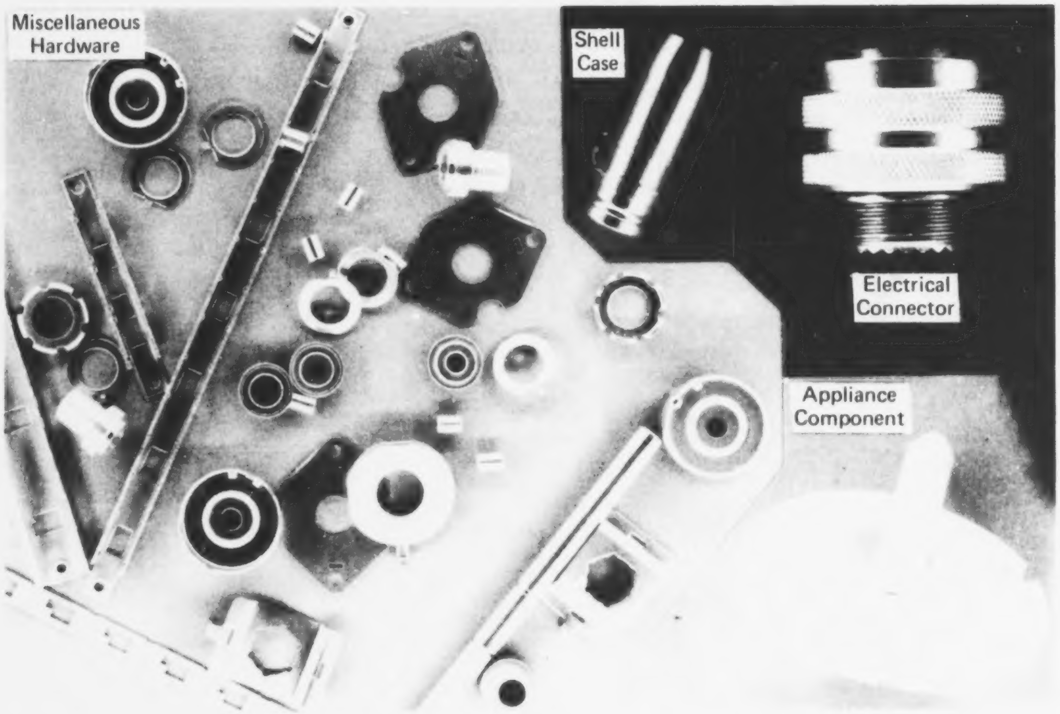


FIGURE 8
IVD ALUMINUM COATED PARTS

Economics of the Coating System

Operating costs of the IVD equipment for the most part can be generalized into three categories–labor, materials and utilities. Labor is the dominant cost factor and each system is designed to be a one man, or less, operation. Materials and utilities costs are a function of coater size and plating requirements, but when combined generally run between $5 and $15 per hour of operation.

In either the barrel or rack coater the plating rate is approximately 0.1 mil per minute.

Plating capacity of a 4 feet by 6 feet barrel coater is approximately 120 pounds of fasteners per hour. Plating capacity for a rack type coater depends upon the size and shape of the parts. A 6 feet by 10 feet coater with a translating evaporation source could coat all of the parts that could be practically racked in one 6 feet by 10 feet plane area. A carriage rack rotating over a fixed evaporation source has higher capacity depending upon part size.

Conclusions

Ion vapor deposited aluminum is a high performance protective coating and is a viable alternate for cadmium plating. It is more compatible with aluminum structure and minimizes the problem of galvanic corrosion when using dissimilar metal fasteners such as stainless steel and titanium alloys. It does not cause hydrogen embrittlement of high strength steel alloys or solid metal embrittlement of titanium alloys. It has a higher useful temperature than cadmium and an all important consideration; it does not contribute to the pollution of the environment.

References

1. MIL-C-5541, Military Specification, "Chemical Conversion Coatings for Aluminum Alloys".
2. MIL-C-83488 (USAF), Military Specification, "Coating, Aluminum, Ion Vapor Deposited".
3. QQ-P-416, Federal Specification, "Cadmium Plating (Electrodeposited)."
4. "Corrosion Performance of New Fastener Coatings On Operational Military Aircraft", Fred H. Meyer, Jr., Edward Jankowsky, International Corrosion Forum, NACE, March 1973.
5. MCAIR M&PD R&D Report No. 118, dated 6 February 1975.

ION VAPOR DEPOSITED ALUMINUM COATINGS

DISCUSSION PERIOD

MR. HRATKO: Bill Hratko, Sundstrand Aviation. I assume the wing skins that you coated were aluminum.

MR. FANNIN: Yes, sir.

MR. HRATKO: What did you gain by coating them with aluminum?

MR. FANNIN: The highstrength aluminum alloys are not really as corrosion-resistant as they should be, and we are putting out a fairly pure aluminum. It is very corrosion-resistant. So we are just replacing a barrier coating with an anodic protective coating.

MR. GEISERT: Ray Geisert, Gould, Incorporated. Gene, did you say that you have the three-tenths mil process pretty much under control now, that you are getting more uniform corrosion results?

MR. FANNIN: Yes. Well, not as well as I would like because I would like to get the 1,000 hours minimum all the time instead of 100, 200, 300. We are consistently able to get the 300 to 336 minimum with the Type II coating, and in a short period of time, I am sure we can double that because the columnar structure that you get is directly related to corrosion resistance, and that can be affected by several things which we are trying to pin down and control during the coating operation.

I can't consistently get three-tenths. We say three-tenths minimum, and we would like to get between three and five-tenths for our fastener applications.

MR. FANNIN: We can probably get only 85 percent of the fasteners in a load to be within that range. Some of them would be higher, and we would rather have them on the high side than on the low side.

MR. TUTTLE: Jim Tuttle, Rust Proofing and Metal Finishing. On the salt spray hours that you referenced in the military specification, was that the acidified salt spray?

MR. FANNIN: No, that is the standard five percent ASD-117.

MR. COLE: Frank Cole, Republic Steel. I have two questions on the process. Number one, how do you handle all that heat of condensation of the aluminum on those thin wing skins?

MR. FANNIN: Very good, and that was a problem. If we go down below, say, a tenth of an inch in gauge thickness, and we don't have much mass to dissipate the heat, overheating can become a problem of aluminum structure, and we are very, very concerned about that, of course.

There are only a few pockets in those wing skins that are less than a tenth of an inch. We have adapted what we call a convection cooling system to our unit, and we will make maybe two quick passes before it will get up to 300 degrees Fahrenheit.

We turn the volts off and we introduce gaseous nitrogen. We cool the parts, and this takes about six minutes. The heavy pumps are still running, the mechanical and the blower, and then we turn the nitrogen off, pump that down to pressure again, and make our second pass.

MR. COLE: I didn't think the skins were that thick. The second question is: What is the material on those bolts or crucibles you use to evaporate the aluminum?

MR. FANNIN: It is a titanium diboride material.

MR. COLE: From Union Carbide?

MR. FANNIN: Well, we have several sources: Union Carbide, Sylvania, and a couple of smaller sources I can't remember right now, but they are basically that type.

MR. KOVELAN: John Kovelan, Diamond Shamrock. Gene, I wonder if you would comment on your throughput or your production capability in numbers.

MR. FANNIN: A good round number, depending on configuration, is about 120 pounds of fasteners per hour. Of course, the big heavy fasteners where you might damage the thread would have to be cooled just a little bit.

MR. SIMMONS: Gene Simmons, Sermetel. Can you tell us what surface finishes are available as coated?

MR. FANNIN: They are about the same as the substrate that you coat. It is a matte finish as coated. I guess I have never checked the RMS of the coating, but it looks the same as the substrate.

MR. SIMMONS: So it is a function of the starting substrate?

MR. FANNIN: Yes. On the barrel coating of fasteners, there is some mechanical pick-up during the tumbling of the barrels, and you get some roughness as a result of that, especially on steel fasteners. On the titanium fasteners, coating is much smoother.

MR. BAYNE: Mike Bayne, Battelle-Northwest. I was wondering what the micro-structure in the "not strictly line of sight" areas was compared to the microstructure in the good line of sight areas.

MR. FANNIN: I don't think I addressed that particular problem. I have seen cross-sections where we would look down inside a hole for example, and see what the thickness was and the taper of the coating. I haven't noticed any difference in the microstructure on a single part, but I guess I have not intentionally looked for a difference.

I wouldn't expect a difference, and it is not one of the variables that we have found necessary to control to get the tightly-knit columnar structure, but that is a good point. I will check that.

MR. BAYNE: Does the columnar structure grow in axis with the crucible?

MR. FANNIN: No, it is generally perpendicular to the substrate.

MR. SARTWELL: Bruce Sartwell, Bureau of Mines. Do you happen to know what the power consumed by your process is in terms of kilowatt hours per square foot?

MR. FANNIN: No, I don't, but we did make a study of the utilities I mentioned, and the cost for electricity was a little better than one dollar an hour for that four by six foot coater, running on a continuous basis.

MR. COOK: I am Albert Cook from the International Lead Zinc Research Organization. I would have to confess to being more interested in the disadvantages of the progress than the advantages. Could you comment on the difference as compared to the cadmium plating, between conductivity, inherent lubricity, galvanic protection, and corrosion resistance? I noticed your corrosion tests related to a large anode, small cathode, large cathode, small anode relationship, where a cadmium plate would show disadvantageously.

MR. FANNIN: We have not found this to be a severe problem in our plasma application which is really the only concern that we have regarding lubricity, the torque-up values that we get. On disassembly we have run a number of tests on reusability with the same results, no problem.

On resistance, the coating, of course, oxidizes as pure aluminum does and has a higher resistance than cadmium, but if you put something like a chromic treatment, one of the MIL-C 55481 treatments that is designed for electric conductivity, you get satisfactory conductivity for grounding applications.

We are looking at this electrical connector possibility now. Whether or not that will work, I don't know. I think it will. Two connector companies have evaluated it and indicated that it will work.

On corrosion, we did an extensive study a few years ago on outdoor exposure of IVD aluminum and cadmium, and the cadmium by its very nature corroded. These were on panels where we stripped different widths of the plating down to the substrata and then exposed them to the outdoor environment, which we classified as industrial environment. The cadmium sacrificed itself in about two years, depending on the width of the strip that was bared, whereas the aluminum did not sacrifice itself, but kept those bare strips from rusting or forming red rust.

I think the IVD aluminum will outlast cadmium because it won't sacrifice itself as quickly. Also, the corrosion products of aluminum are not as detrimental as the corrosion products of cadmium, in my opinion.

MR. COOK: I think a careful assessment of the specific application is needed to determine whether the galvanic aspects are important or not. If they are, then, of course, cadmium would be more beneficial.

MR. FANNIN: We let the people that want to use the coating evaluate it for their own application. We do not evaluate.

MR. COOK: I would be very concerned about jamming possibilities for this new coating and certainly electrical resistance for electronic applications.

MR. FANNIN: You can bet that we thoroughly evaluate it before it is used.

MR. LEVY: Don Levy of Lockheed Palo Alto Research Labs. Is there any particular problem with coating inside of the cavities, other than the normal problem with small-diameter, very deep holes?

MR. FANNIN: Well, yes. If you get a deep enough cavity, and under certain configurations you can create a hollow cathode which would be very damaging to parts adjacent to where the ions were coming out, where you are concentrating ions, so we are very careful about coating parts such as that. We would block off the hollow material.

We cannot coat the gear of the landing gear, but we can coat a blind hole, that's in the landing gear, or the lugs where they have holes.

MR. LEVY: Is there some dimensional limit that gives you this problem?

MR. FANNIN: Well, as far as corrosion is concerned, we tell our designers that we will not uniformly maintain more than one diameter in depth, and beyond that it starts to taper off. It's very much like cadmium, back cadmium, or the low brittling cadmium, as far as throwing power is concerned.

MR. ISLER: William Isler of Diamond Labs. The heating problem that you mentioned for the thinner pieces, was that source of heat primarily your discharge system or your evaporative system?

MR. FANNIN: There are three areas where you get heat buildup. In the order of magnitude, the glowdischarge is least, the radiation is second, and the heat of condensation is the bulk.

MR. ISLER: Is the glowdischarge power level the same during cleaning as during deposition?

MR. FANNIN: Yes.

MR. ISLER: Do you have another source of ionization besides the glowdischarge system?

MR. FANNIN: No, sir.

I might add that sometimes during evaporation, I guess the conductivity within the system changes within the plasma and sometimes the potential does drop off, and if you want to maintain a constant potential or a constant current density, you have to adjust the voltage.

MR. WHITE: Marty White, Cadmium Association.

Have you done any work on the deposition of aluminum on sintered metal components, and, if so, what sort of theory could you come up with?

MR. FANNIN: We are presently using the IVD coating for some tungsten alloy steels that are sintered metal.

MR. WHITE: Have you any idea what the theoretical density on this component is?

MR. FANNIN: No, I have not. They are very heavy.

MR. LAZARZ: Mark Lazarz, Cutler-Hammer.

Have you tried using IVD on copper substrate?

MR. FANNIN: Not for a functional application. We have used copper in some of our development work, mainly to evaluate the effect of glowdischarge cleaning, current densities and so forth, because you can oxidize copper readily and see the effects.

MR. FANNIN: There is no problem getting adhesion of aluminum on copper by this process, or any other conductive substrate of which I am aware.

MR. LAZARZ: What about diffusion?

MR. FANNIN: You can get diffusion, but there is no diffusion that I can detect with the laboratory techniques that we have applied. There are people evaluating it as a replacement for pack cementation or high temperature applications on engines. We can get a fairly uniform aluminum coating, and the diffusion is more uniform. Aluminum will diffuse in most iron-based and nickel-based alloys.

Alternative Materials and Processes

Session II

Tuesday Afternoon 1:45

CADMIUM IN FOOD AND DRINKING WATER - FDA CONSIDERATIONS

Samuel Shibko
George L. Braude
Division of Chemical Technology
Public Health Service
Food and Drug Administration
Washington, D.C. 20204

Cadmium in waste discharges from plating plants may enter the food chain directly via drinking water, or indirectly through crop irrigation and use of sewage sludge on agricultural land.

The average human intake of cadmium in the U.S. is approaching maximum levels recommended by the World Health Organization. Most of this intake comes from food and water, especially for non-smokers. Different types of foods vary greatly in their cadmium levels. Large differences also exist in the total contribution each food group makes to the daily intake of this toxic metal.

Long term hazards of cadmium to humans are due to the insidious nature of this element. Accumulation in the body is gradual and occurs even at relatively low exposure levels over many years.

CADMIUM IN FOOD AND DRINKING WATER - FDA CONSIDERATIONS

By

Samuel I. Shibko and George L. Braude

Bureau of Foods
Food and Drug Administration
200 C Street, S. W.
Washington, D. C. 20204

In talking to a group of people who are involved in electroplating like yourself, the question obviously arises: what is the relationship between what you are doing and cadmium in food and water? The answer is that use of cadmium in electroplating is one of the factors, probably a major factor, which will determine whether the exposure of the general population of the United States to this toxic element will be increasing or decreasing in the years to come.

Let us first examine what happens when cadmium is allowed to enter a plant's waste stream. If the outlet "pipe" leads to a municipal sewage treatment plant, cadmium, with other waste materials, will be processed by one of the several sewage treatment processes now in use. The result will be that at least 50% of the total amount of cadmium present will be precipitated or adsorbed and remain with the sewage sludge. The balance of the cadmium which was introduced from the industrial activity or which was present in water or other sewage components will remain in the effluent water. The effluent in turn may be discharged to a river or lake and thereby form our raw water supply for municipal drinking or industrial use water or it may be used in agriculture as irrigation water.

Sewage sludge can be disposed of in landfills, it can be incinerated, or used in agriculture as fertilizer and mulch. We are going to discuss this latter use, which is of considerable importance in reviewing the fate of cadmium in the environment and in the food chain later. But, first, let us consider the possible effects on the levels of cadmium in food and water of that portion of the cadmium which remains in the effluent which usually enters rivers and lakes. When such water is used as a source of drinking water, regulations promulgated by the Environmental Protection Agency will apply. These specify that such water shall not contain more than 0.01 milligrams of cadmium per kilogram of water or 10 parts per billion. Most potable water supplies in the United States are well below this limit (though a few exceed it at times) and it would be very unfortunate if significant increases were to occur. Then there is the problem of the possibility of accumulation of cadmium in edible aquatic species. Studies indicate that cadmium accumulation in fish occurs primarily in kidney, liver, gill and the gut with lesser amounts in bone and muscle. Accumulation occurs through exposure to cadmium dissolved in the water, rather than the intake of cadmium-containing food, i.e., it is likely that there is no marked food chain accumulation of this element and that the high levels of cadmium observed in fish from contaminated areas are due to direct concentration from water (1). The greatest concentration of cadmium is observed in estuarine species, primarily shellfish, where concentration factors - based on a sea water concentration of 0.1 ppb - range from 1000 - 14,000 (2). There is also the ecological concern that if cadmium pollution in freshwater areas is high enough, it may eliminate the normal aquatic life completely. These ecological problems will be discussed in detail tomorrow.

Reproduced from
best available copy.

Water is also used extensively in the South West and in California and other arid or semi-arid areas to irrigate a variety of crops. The cadmium, being readily available in soluble form, is taken up by the crops planted, and becomes part of the plant and, if these are food plants, of the human and animal food chains. Cadmium in normal irrigation water may be limited to acceptable levels. Of most concern, however, is the presence of excess cadmium in sewage sludge (3,4). The Federal Water Pollution Control Act in 1972 (PL 92-500) mandates that all municipal sewage will have to undergo at least secondary treatment. An extensive building program is underway, largely financed by the government, to construct sewage treatment plants all over the United States, or provide secondary and sometimes tertiary treatment facilities for existing plants. The results will be cleaner rivers and lakes, but also vast and increasing quantities of sewage sludge. This sludge has to be disposed of, and with strict limitations on ocean dumping and incineration, land application is becoming a logical alternative. To make such land application economical it must be used on land where crops are being grown which in many cases are destined for human or animal consumption.

The cadmium content of sewage sludges ranges, on a dry weight basis, from a few parts per million (ppm) to several thousand ppm. Many large and small cities produce sludges in which the cadmium levels exceed 100 ppm, while other municipalities of similar size have relatively low levels of cadmium, often below 10-15 ppm. The difference is the input from industrial effluents, including electroplating.

Table 1 shows what happens when crops are grown in soil to which sludge containing excessive amounts of cadmium had been applied. As you will notice, the cadmium content of all the crops has increased greatly as compared to the controls, which were grown in soil fertilized with ordinary fertilizer. Leafy vegetables, forage for domestic animals and some grains are especially likely to accumulate excessive quantities of cadmium, when planted in sludge-amended soils. Over the last several years, much research has been conducted, some supported by FDA, to define the variables affecting the uptake of cadmium and other metals by food crops (5). It has been shown that many factors are involved, including types of soils and pH, rates and timing of sludge applications, interaction of cadmium with other elements (especially zinc), type of crops planted and their age, etc. It is possible to reduce the level of cadmium uptake by crops by good agricultural practice, including liming and selection of those crops which are less likely to accumulate this element. However, when large amounts of high cadmium sludges are used, crops will nearly always show increased cadmium concentrations in plant tissues, including the edible parts.

The question may be asked, why should we be concerned about low levels of cadmium entering our food supply? The concern is two-fold. First, there is the available information on the possible toxic effects of chronic low level exposure to cadmium and secondly, the information on the present level of exposure of the general population of the U. S. to cadmium from food.

Reproduced from best available copy.

First, I will discuss the toxicological information. Cadmium is generally considered to be a non-essential element, i.e., it has no known function in living systems. In mammals it is essentially absent at birth but accumulates in the body primarily in the liver and kidneys during a lifetime. Although only a small amount of ingested cadmium (between 4 - 7.0%) is retained, only a very small percentage of the daily absorbed dose will be excreted. Thus, there will be considerable accumulation with time even at relatively low dose levels. Exposure to high concentrations of cadmium in the air, in the industrial setting, is characterized by anemia, damage to the lungs, and kidney damage which is characterized by the excretion of low molecular weight proteins commonly characterized as tubular proteinuria. Cadmium poisoning had previously been thought of as primarily an industrial exposure problem.

However, the identification of cadmium as one of the causative factors of the so-called Itai-Itai disease, reported from Japan in the '60s although it was probably occurring at a much earlier date in the affected areas, indicated the possibility of the types of problems that could arise for the general population if widespread contamination of the environment with cadmium occurs. The cadmium contamination in this incident was due to a mining operation which polluted river water used for irrigation of the rice fields. The Itai-Itai disease was associated with the ingestion of the cadmium-contaminated rice by a particularly sensitive population, deficient in both calcium and Vitamin D. In general, the typical cases reported consisted of women more than 40 years old and with multiple childbirths. The disease is characterized by severe osteomalacia or bone softening leading to multiple fractures. Kidney damage (tubular proteinuria) of the same type as that observed in industrially exposed workers was also found. The cadmium intake was estimated to be 600 µg/day, which is 10 times higher than that in the non-contaminated areas. The cadmium in irrigation water in this area reached a concentration of up to 0.09 mg/l. Vegetation grown in fields served by the contaminated water had high levels of cadmium, e.g., rice 0.44 - 3.6 ppm and soybean 1 ppm, and must have been the major source of the intake of cadmium by the affected individuals.

The first detailed review and evaluation of the problem of estimating tolerable levels of exposure of the general population to cadmium was published by Professor Friberg and his co-workers at the Karolinska Institute, Sweden in 1970 under a contract between the U. S. Environmental Protection Agency and the Department of the Environment of the Karolinska Institute (6). The most important considerations in this evaluation were (a) cadmium has an extremely long biological half life in man, (b) low level exposure to cadmium with time results in considerable accumulation of cadmium in the kidney, (c) the critical level of cadmium in the cortex of the kidney (based on animal studies and human autopsy data) associated with development of long lasting proteinuria, i.e., kidney damage, is about 200 ppm wet weight, (d) the present mean levels in the kidney cortex in 50-year old people not known to be exposed to excessive amounts of cadmium are 25 - 100 ppm, and these levels were obtained by daily intakes of cadmium varying between 25 - 100 µg, (e) it was calculated that the necessary daily intake of cadmium from food to reach the critical kidney cortex concentration over a 50-year period would be 250 - 350 µg. (Table 2)

In 1972 the WHO/FAO examined the available data, and concluded that the maximum level of cadmium that can be considered tolerable by man within the present state of knowledge is 400-500 micrograms per week, (equivalent to 57 to 71 micrograms per day)(7). Recently, Kjellstrom has published the results of his studies with cadmium-exposed Swedish workers and Japanese farmers, using the range of exposure levels and duration of urinary excretion of a specific protein associated with kidney damage. The results support the previous assumption that the critical concentration of cadmium in the kidney cortex is 150 - 300 µg cadmium/g (8,9), and this provides additional support for the low margin of safety of the present daily intake of cadmium and levels that could cause minimal toxic effects. Again, I would emphasize that the concern for exposure to cadmium from food is not the acute and rapid poisoning, but the effects due to chronic low level exposure which is slow and insiduous, requiring many years, 20 or 30 or more, until the deleterious effects manifest themselves.

Now that I have discussed the hazard associated with chronic exposure to increased levels of cadmium, it is important to relate this to present day levels of cadmium in the diet. The present average dietary intake of cadmium in the United States is about 72 µg/day, and thus either is approaching the tolerable daily intake or may already have reached it.

The basis for these intake values are the Total Diet Surveys, which are conducted by the Food and Drug Administration (10,11). These surveys, which are also called the Market Basket Studies, have been performed annually since 1965. They are based on food consumption information developed about 10 years ago by the U. S. Department of Agriculture and correspond to the diet of a 15 to 20-year old male, the heartiest eater. A total of 117 different foods are included and the foods are cooked or otherwise prepared as normally eaten. The 117 foods are divided into twelve different food class composites which are analyzed for the various contaminants. The total intake, including drinking water, is about 3,000 grams per day.

In the overall exposure of urban populations to cadmium it has been estimated that foods provide roughly 80-85%, drinking water 15-20%, and airborne contaminants 1% of this element (12). In addition, an average smoker is expected to be absorbing an additional 15-20 micrograms per day from the tobacco smoke by inhalation.

The cadmium content of the various foods differs greatly, even though grown on ordinary (not sludged) soil. Highest cadmium concentrations can usually be found in some leafy vegetables, grains and fruits.

Reproduced from
best available copy.

However, because of the magnitude of the intake of, for instance, the grains, their contribution to the total dietary intake of cadmium presents a somewhat different picture, as shown in Figure I. Here, grains, vegetables, potatoes and fruits make the largest contribution.

In the total diet survey and in other studies of a similar nature which are conducted by FDA, we are usually dealing with the "average person." However, there are population groups in the United States which because of dietary habits or preferences are exposed to both higher and lower cadmium levels. Vegetarians, especially strict vegetarians who exclude meat, milk and eggs, consume large amounts of those food items which may be cadmium cumulators, such as grains, green vegetables, and various nuts and seeds. There is no survey available which has measured the cadmium intake of vegetarians as yet. However, estimates have been made which show the possibility of potentially increased exposure to cadmium compared to that of the general population (13).

The Food and Drug Administration is concerned that the level of cadmium in our present diet is close to or has reached the tolerable limits established by the WHO/FAO. In order to minimize any potential increase in dietary intake of this toxic element, consideration is being given to establishing tolerances or guidelines for cadmium in various foods. However, cadmium is naturally present at low levels in our soils, in water and food and even in the air. It has been properly defined as the dissipated element (14). The Food and Drug Administration is now conducting annual surveys of raw agricultural commodities, which are being collected in different parts of the United States and analyzed for cadmium, lead and zinc. This will provide the baseline needed so that, if considered desirable and feasible, limitations or tolerances can be developed in the future. However, even if limitations were available, controls will still have to be exercised at the source prior to the introduction of this toxic element into soils and water and ultimately into human and animal food. Substantially reducing the amount of cadmium entering the environment from electroplating plants is a major step towards the control of this problem. This is the reason why this conference is so valuable, as it may help reduce the widespread distribution of cadmium from industrial processing and provide for better and safer food and water.

REFERENCES

1. Landner, L., and Jernolov, A. (1969). Cadmium in Aquatic Systems. In Metals and Ecology, Symposium, Stockholm 1968. Ecological Research Committee Bulletin No. 5. Swedish National Science Research Council. Sveavagen 166 VIII, S-133, 46, Stockholm, Sweden.

2. Pringle, B. H., and Shuster, C. N. (1968). A Guide to Trace Metals in Shellfish. 1968 Workshop. N. E. Shellfish Sanitation Research Center, Shellfish Sanitation Branch.

3. Braude, G. L., Jelinek, C. F., and Corneliussen, P.: "FDA's Overview of Potential Health Hazards Associated with the Land Application of Municipal Wastewater Sludges". Proc. of the 1975 Nat. Conf. on Mun. Sludge Mgmt. and Disp., Aug. 18-20, 1975, Anaheim, Cal.

4. Jelinek, C. F., and Braude, G. L.: "Management of Sludge Use on Land; FDA Considerations Proc. of the 3rd Nat. Conf. on Sludge Mgmt. Disp. and Utiliz., Dec. 14-16, Miami, Fla.

5. Chaney, R. L., Hornick, S. B., and Simon, P. W. "Land as a Waste Management Alternative", Proc. 8th. Ann. Waste Man. Conf., Rochester, N. Y., 1976.

6. Friberg, L., Piscator, M., Nordberg, G. F., and Kjellstrom, T. (1974). Cadmium in the Environment. Published by CRC Press Inc., Cleveland, Ohio.

7. 16th Report of Joint FAO/WHO Expert Committee on Food Additives, Geneva 1972.

8. Kjellstrom, T., Evrin, P.-E., and Rahnster, B. (1977). Dose-response relationship of cadmium-induced tubular proteinuria. A study of workers exposed to cadmium in a Swedish battery factory. Env. Res., 13(2), 303.

9. Kjellstrom, T., Shiroishi, K., and Evrin, P.-E. (1977). Urinary β_2-microglobulin excretion among people exposed to cadmium in the general environment. An epidemiological study in co-operation between Japan and Sweden. Env. Res., 13(2), 318.

10. FY 73 Total Diet Studies, No. 7320.08 Bureau of Foods, FDA, Jan. 9, 1975.

11. FY 74 Total Diet Studies, No. 7320.08 Bureau of Foods, FDA, Jan. 21, 1977.

12. Compliance Program Evaluation, FY 1974, Heavy Metals in Foods Survey 732-136. Bureau of Foods, FDA, June 19, 1975.

13. Braude, G. L., and Jelinek, C. F. "FDA's position on municipal sludge application on agricultural land." Presented at 1977 Summer Meeting of the American Society of Agricultural Engineers, Raleigh, N. C., June 26-28, 1977.

14. "Cadmium, the Dissipated Element", Ed. by William Fulkerson, H. E. Goeller ORNC-NISF-EP21, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830, Jan. 1973.

15. Giordano, P. M., and Mays, D. A. "Biological Implication of Metals in the Environment", 15th Ann. Hanford Life Sci. Symp., Richland, Wash. (in press).

TABLE I CADMIUM CONTENT OF CROPS GROWN ON SOIL WITH AND WITHOUT ADDED SLUDGE PPM, DRY MATTER BASIS

Crop	Soil	
	Sludged	Not Sludged
Soybeans[a]	3.7[c] 1.5	0.4[c] 0.3
Oats[a]	2.1[c] 0.4	0.2[c] 0.04
Swiss Chard[a]	73.0[c] 5.5	3.6[c] 1.2
Tomatoes[b]	1.1	0.3
Squash[b]	0.7	0.3
Lettuce[b]	7.0	1.2

---

a) Chaney, *et. al.* (5)

b) Giordano, *et. al.* (15)

c) Soil pH <5.3; all other >6.4

Table II

Factors considered for evaluating tolerable daily intakes of Cadmium.

(1) Cadmium has an extremely long biological half life (18-35 yrs).

(2) Low level exposure to cadmium with time results in considerable accumulation of cadmium in the kidney.

(3) The critical level of cadmium in the cortex of the kidney associated with development of long lasting proteinuria, i.e., kidney damage is about 200 ppm wet weight.

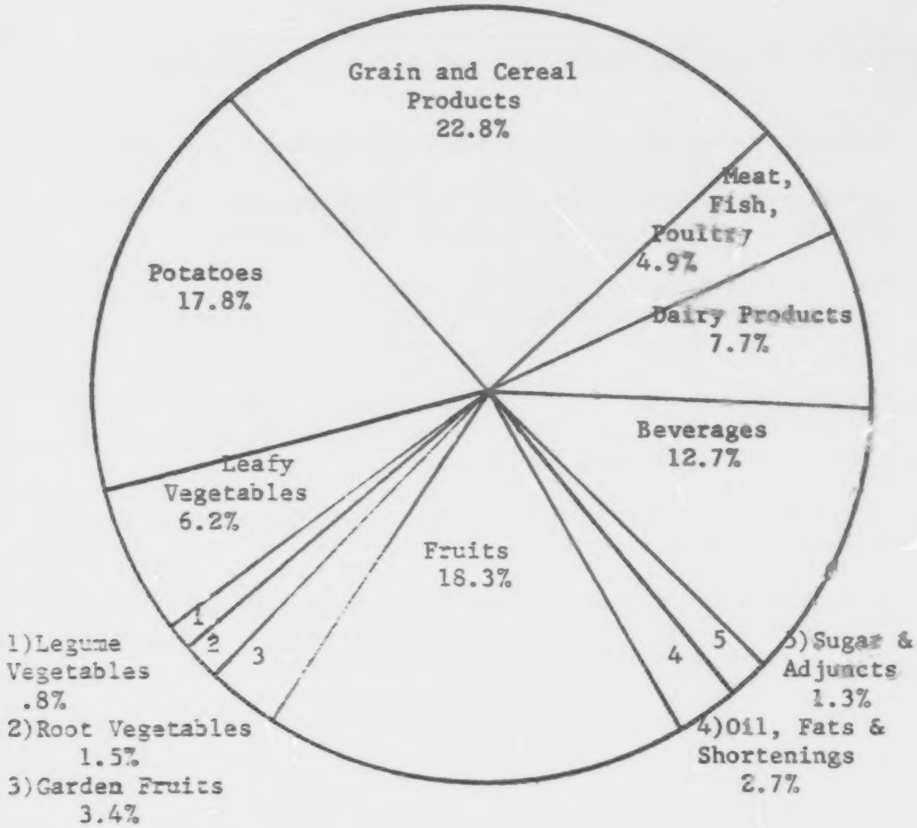
(4) The present mean levels of cadmium in the kidney cortex in 50-year old people not known to be exposed to excessive amounts of cadmium are 25-100 ppm.

(5) The levels were obtained by daily intakes of cadmium varying between 25-100 µg.

(6) It was calculated that the necessary daily intake of cadmium from food to reach the critical kidney cortex concentration, over a 50-year period would be 250-350 µg.

Fig. I

Contribution of Food Groups to Cadmium Intakes



DISCUSSION PERIOD

MR. YOST: Jack Yost, Purdue University.

Dr. Shibko, you emphasized that the cadmium contents of various classes of foodstuffs vary markedly and that this might impact on various ethnic groups who consume one type of food to the exclusion of other types of foods. Have you made any studies at FDA on the dietary habits of various population, ethnic, or socioeconomic groups?

DR. SHIBKO: So far at FDA we have not carried out the study although we are aware of the problem. I think the MRC is presently carrying out various detailed surveys we hope to use in order to get better information so we can see which groups of individuals will be greater risks.

As you may know, the USDA is also about to undertake a new survey of dietary habits of the general population and this probably will be a much larger survey than the one which was previously carried out in 1965. In that survey, I think the eating habits of individuals were studied for only a single day, whereas, in this new survey, the eating habits over a period of three days will be studied with particular attention to the various ethnic groups.

MR. LYMAN: Don Lyman of the International Lead Zinc Research Organization. Two months ago in East Germany, Harlan, et al, of FDA presented a paper on "Cadmium in the American Diet," in which they said there had been fluctuations in cadmium levels in diet through the years, but there had been no detectable trend indicating increased levels of exposure to cadmium in food. I think they were referring to the market basket surveys.

MR. LYMAN: Based on these considerations, the present levels of cadmium in food do not pose a toxicological problem to man. However, continued monitoring of the food supply for cadmium trends is necessary.

You seem to paint a much darker picture.

DR. SHIBKO: There is a very small margin of safety between what man is presently exposed to, and the levels that cause the minimum toxic effects. We are very anxious to insure no increase in the general level of cadmium in the food supply.

MR. LYMAN: But evidently there is no evidence to indicate that there has been an increase in cadmium in foods.

DR. SHIBKO: No, but we feel that the possibility of the use of large amounts of cadmium-containing sewage sludge, particularly on certain crops, could result in a dramatic increase in the levels of cadmium in food supplies, which would be reflected in the levels of cadmium in the total diet.

MR. LYMAN: But actually there has been no indication to date?

DR. SHIBKO: No, this has not occurred so far and I don't think that the present use of cadmium sludge is very wide-spread in this country. It's in the experimental stage.

MR. GLEASON: Tom Gleason of EPA.

If you take the 33-microgram value that was quoted, the mean average of all the values that FDA has compiled since 1967, this will give you this particular value. But, you have to consider the lower accuracy of the methods used in earlier surveys and the small safety factor in using the WHO tolerance level.

DR. SHIBKO: I think it is very important to consider all or much of the earlier analytical studies in view of the very difficult problems in analysis.

Alternative Materials and Processes

Session II

Tuesday Afternoon 2:20

CADMIUM PLATING WITH ENVIRONMENTAL RESTRICTIONS

L. E. Vaaler
J. Gurklis
BATTELLE - Columbus Laboratories
Columbus, Ohio 43201

From a practical standpoint it must be assumed that cadmium is toxic at extremely low concentration levels. However, cadmium electroplate is very useful and is required for specific applications. For protective coatings on gray iron castings, cadmium is considered indispensible by many authorities. Corrosion products of cadmium are less voluminous than those of zinc and less likely to interfere with the function of moving parts. Cadmium corrodes at a much slower rate than zinc in marine atmospheres. A coating composite of tin over cadmium has a durability and service life under some conditions that is not equalled by a single metal or other simple composite, including tin-zinc. Therefore, the problem is to electroplate cadmium and still satisfy the environmental restrictions.

Specifically tailored recovery methods, provision for handling spills, segregated treatment of unavoidable waste-water, and careful control of the complete operation will be required. With these requirements cadmium should be plated only in installations that specialize in it and that have sufficient production volume to justify the appropriate control procedures. Cadmium plating as an intermittently used process in a general plating shop will not be economically feasible.

The paper discusses the technology and estimated costs as a function of production volume for plating cadmium under the restrictions that will probably be imposed.

Preceding page blank

CADMIUM PLATING WITH ENVIRONMENTAL RESTRICTIONS

J. A. Gurklis and L. E. Vaaler

INTRODUCTION

This conference on cadmium is one of an increasing number of discussions on substances or processes known to be or suspected of being harmful to the environment. The ideal goal is to completely eliminate the substance or processes in question and find completely satisfactory and safe alternatives for all applications. Another possible temporary goal, however, is to contain the substance in manufacture and use.

We believe that a practical objective for cadmium is to find substitutes where it is possible, technologically and economically, and to practice containment where the properties of cadmium lead to unique applications.

Special Uses of Cadmium

The performance of cadmium has often been compared with that of zinc, which has similar properties and chemistry and is cheaper and more acceptable to the environment. There is evidence that cadmium affords better protection to steel in humid, tropical, and certain marine environments, and provides a more integral plate on cast iron than does zinc. Cadmium appears more suitable than zinc for soldering operations, for making electrical contacts, and for providing a low coefficient of friction. However, one should not be too dogmatic in citing unique uses. From a practical standpoint, it is not possible to find a substitute for cadmium plate in a relatively short time for many manufactured items. The field testing and changing specifications can require years before the modified product can be sold or used with confidence. We have personal experience with this situation. From published results it appeared that a tin-zinc alloy plate might be used for components in an assembly that were normally plated with cadmium and tin. However, accelerated corrosion tests did not support the substitution. Perhaps the substitution would have been satisfactory under actual conditions of use but there was certainly no rationale for risking such a change.

Containment of Cadmium-Analogy with Mercury

As a precedent for using and containing cadmium, the situation with mercury can be considered. Mercury came under scrutiny as the result of adverse consequences of its release into the environment in Japan and Sweden and determination of high levels in fish in the Great Lakes. Mercury is used in large amounts for a flowing cathode in chlorine-caustic production. The result of environmental limitations in the U.S. was: (1) the phasing out of old, inefficient plants for which a substitute technology was available, (2) no sales of new mercury cathode cells, and (3) development of methods of mercury containment for modern mercury cell installations. In Japan a deadline was set for elimination of mercury cells, but the huge cost of such a replacement and the development of more efficient methods of mercury containmnet has caused MITI to have second thoughts about following through on this.

Specializing in Cadmium Plating

Although cadmium plating is frequently included as a routine operation in typical job shops, some shops have now eliminated cadmium. They have found that the amount of business derived from cadmium plating is not worth the trouble and cost of meeting present and anticipated pollution requirements. However, it is reasonable to assume that with some critical size and continuity of operation plating and containment operations can be justified.

A couple of examples will be used to approximate the cost of a modest-sized cadmium line which is operated at full capacity and uses a recovery technique to minimize waste. The first example will use evaporative recovery. A two-stage (double effect) recovery unit will be assumed rather than the more common single stage unit in order to save steam (energy).

The second example will assume reverse osmosis recovery in place of evaporative recovery. This technique is less established for cadmium cyanide baths than is evaporative recovery. Nevertheless, it is a very promising method that will probably be established in the future.

To provide a basis for modelling and costing a recovery system, a plant producing 2,000 sq ft/day (186 sq m/day) of cadmium plate will be assumed. An outline of the process steps and volume of rinse water used is shown in Table 1.

The amount of dragout from a cadmium plating bath is important in establishing the economics of a cadmium plating recovery and waste treatment system. We have assumed dragout values of 5 gallons/1000 sq ft (0.2 liter/sq m) for barrel plating and 3 gallons/1000 sq ft (.12 liter/sq m) for rack plating to be typical. Of the 2,000 square feet (186 sq m) of plated product, 2/3 of the area is barrel plated and 1/3 rack plated. The average dragout for the daily production is then 4.33 gallon/1000 sq ft (0.18 liter/sq m).

The volumes of rinse water going to treatment or recovery were calculated using ideal mixing formulae modified by an efficiency factor of 50 percent. This means that if the desired concentration of chemicals in the final rinse assuming ideal mixing is, say 15 ppm, the dragout film on the part will be of this concentration but the rinse water itself will have a concentration of only 8 ppm and will be twice the volume of rinse water needed than if ideal mixing occurred.

Cadmium Plating with Evaporative Recovery

An evaporation of 50 gal/hr (189 liters/hr) will handle the daily 400 gallon (1514 liters) for the cadmium rinse in 8 hours. Cost estimates for purchase, installation, and operation of a two-stage 50-gallon evaporative recovery unit are given in Table 2.

Recovery by Reverse Osmosis

Evaporative recovery is an established technique for cadmium cyanide baths. Reverse-osmosis with this bath is less well developed and there is promise that suitable membranes are or will soon be available to make it practical. There is also promise that reverse-osmosis will be cheaper and less energy consuming than evaporative recovery. Therefore, costs have been projected for this system in Table 3, even though it is not an established technique.

TABLE 1. PROCESSING STEPS FOR CADMIUM PLATING

Process	Bath Composition		Time, min	Solids Conc(1) in Final Rinse, ppm	Actual Rinse Water Use, l/day
	Item	Concentration, g/l			
Anodic alkaline clean	Alkaline salts	60	1.25	--	--
Single rinse	--	--	.75	750	5246
Acid pickle	HCl	111	1.00	--	--
Double countercurrent rinse	--	--	1.25	750	797
Caustic dip	NaOH	15	1.00	--	--
Double countercurrent rinse	--	--	0.75	50	1135
Cadmium plate	Cd	20	20.0	--	--
	NaCN	100			
	NaOH	14			
	Na_2CO_3	52			
Triple countercurrent rinse	--	--	2.25	15	1518
Chromate dip	$Na_2Cr_2O_7;2H_2O$	15	0.5	--	--
	HNO_3	7.5			
Double countercurrent rinse	--	--	6	37	779

(a) This value is for ideal mixing where rinse water volume would be half of actual use.

TABLE 2. COSTS FOR EVAPORATIVE RECOVERY OF CADMIUM CYANIDE SOLUTION DOUBLE-EFFECT 50 GAL/HR UNIT

Item		
INVESTMENT COSTS		
Purchase Cost		$30,000
Cost of Installation and Auxiliary Items		10,000
OPERATING COSTS		
Interest/Year (10 percent)		2,000
Depreciation/Year (20 percent)		8,000
Steam at $4.00/1000 lb., 800,000 lb.		3,200
Electricity at 4¢/kwh, 42000 kwh		1,680
Labor at $12.00/hr, 240 hrs		2,900
TOTAL OPERATING COSTS		$17,780
Area Plated/year (240 days)	480,000 sq ft (44,600 sq m)	
Recovery Unit Cost	$.037/sq ft ($0.40/sq m)	

TABLE 3. COSTS FOR RECOVERY OF CADMIUM CYANIDE PLATING SOLUTION BY REVERSE OSMOSIS

INVESTMENT		
Cost		$20,000
OPERATING COSTS		
Interest/Year on Initial Cost (10 percent)		1,000
Depreciation/year (20 percent)		4,000
Electric (50 kwh/day)		500
Maintenance (5 percent)		1,000
Membranes		1,500
TOTAL OPERATING COST		$8,000
Area Plated/Year	480,000 sq ft (44,600 sq m)	
Unit Recovery Cost	$.017/sq ft ($.18/sq m)	

Savings in Chemicals by Use of Recovery Systems

Without a recovery system the amount of solution dragged out of the plating bath annually is:

(4.33)(500) = 2165 gallons (8200 liters).

The saving in chemicals by use of a recovery system is a credit against the cost of operating the cadmium system itself. The amounts of chemicals lost in this way and their cost are shown in Table 4. Furthermore, chemicals are required to treat this dragout and are also included in Table 4.

Treatment of Cadmium Wastes

Even with a recovery system, waste water and other solutions requiring treatment to remove cadmium (and possibly other metals) can come from:

1. Rinses following chromating
2. Dumping of the chromating solution
3. Purging of the plating-recovery loop or other losses from this system.

The cadmium dragged out of the cadmium rinses into the chromating system is only 0.5 g/day (8.66 gallons or 33 liters/day containing 8 ppm of cadmium). If the chromating solution has a volume of 200 gallons (757 liters) and is dumped every 10 days, the average volume/day of waste chromating solution plus chromate rinse water is 20 + 206 = 226 gal (856 liters). The average concentration of cadmium in this wastewater (assuming the work is not significantly etched in the chromating bath) is 0.6 ppm. Chromium concentration assuming no loss from chromating would be 480 ppm.

Directing the wastewater and purge from the cadmium line to the plating chemical waste treatment system will dilute the cadmium in a larger volume. Even after treatment to precipitate as much cadmium as possible the total cadmium discharged in the effluent may be larger than if the water from the cadmium line were treated separately. A separate waste treatment system would gain some economics from sharing personnel, testing, and possibly some control equipment with the larger treatment facility but could cost from $25,000 to $50,000 and increase production costs up to $.05/sq ft.

TABLE 4. CHEMICALS CONSERVED WITH A RECOVERY SYSTEM

Process	Chemical	Annual Loss or Use, kg	Unit Price $/kg	Total Saving, $
Dragout	Cadmium	164	8.25	$1,356
	Sodium Cyanide	820	1.00	820
	Sodium Hydroxide	115	.60	68
	Sodium Carbonate	426	.44	188
Chemical	Chlorine	2968	.18	534
Waste Treatment	Sodium Hydroxide	564	.60	338
TOTAL				$3,304

If the main treatment plant operates in a batchwise mode it can be suggested that cadmium-containing waste be collected in a holding tank to a volume sufficient for batch treatment. This can then be transferred to the main plant for separate treatment, thus avoiding dilution with other waste water.

Other end-of-pipe treatments for the small amount of cadmium-containing wastewater from the plating line can be suggested but we will not speculate further. It may be concluded that cadmium plating with containment is possible with a moderate economic premium, providing a full production schedule can be maintained.

Alternative Materials and Processes

Session II

Tuesday Afternoon 2:55

OUTSTANDING CORROSION PROTECTION WITH ZINC FLAKE IN A WATER-BASED COATING

Jon A. deRidder
John R. Kovelan
Diamond Shamrock Corporation
Metal Coatings Division
Chardon, Ohio 44024

A new and cost competitive, corrosion-resistant coating for ferrous and other substrates has been commercialized. The coating, developed and marketed by Diamond Shamrock Corporation, is a new addition to their family of corrosion-protection systems. The coating contains zinc flake, chromium and proprietary organics in an aqueous dispersion. Applied by immersion, the coating is essentially inorganic after being baked to an adherent, metallic gray finish. The average dry film thickness is 5.0 - 8.0 microns which is equivalent to a coating weight of 1500-1800 mg per square foot.

Outstanding corrosion resistance is obtained by the combination of barrier protection and controlled cathodic protection afforded by the zinc flake, which is passivated and bonded by the chromium. The coating is also completely resistant to solvents, gasoline and brake fluids and will withstand temperatures in excess of 300°C.

Unlike cadmium, the coating application process is completely free of hydrogen embrittlement and pollution, in that is uses no acids, electrolysis, or post rinses.

The main users to date have been the U.S.A. and Japanese automotive, appliance and building industries. Chrysler Corporation, General Motors Corporation, General Electric Company, Nissan Motors and Toyota have issued specifications. The coating is currently being used to protect fasteners and other small metallic items, although larger parts and assemblies can be rack-coated using an overhead conveyor system.

OUTSTANDING CORROSION PROTECTION PROVIDED WITH ZINC FLAKE IN A WATER-BASED COATING

J. A. deRidder and John R. Kovelan

Diamond Shamrock Corporation
Metal Coatings Division
P. O. Box 127
Chardon, Ohio 44024

A new corrosion-resistant coating for ferrous and other metal substrates has been commercialized. The coating, developed by Diamond Shamrock Corporation, is a new addition to their family of corrosion protection systems. The coating is marketed by Diamond Shamrock and its Joint Venture Companies, Nippon Dacro Shamrock in Japan and Dacral in Europe.

The Coating

The coating, as applied, looks very much like zinc plate, but it is not a plating. The coating is applied by immersion and then baked to an adherent metallic gray finish, which is essentially inorganic.

By definition, the coating is an aqueous dispersion of zinc flake, containing chromium and proprietary organics. The organics are used to derive the proper chemistry during the bake operation and then are essentially destroyed at the peak metal temperature. (Slide #1)

The most unique physical aspect of the coating is that it contains zinc flake. The zinc flake is typically 0.2μ-0.4μ thick and averages 20μ-30μ in length. It becomes obvious that with reasonable orientation, a small amount of zinc flake will cover a large surface area as compared to zinc dust. (Slide #2)

The applied coating has a typical dry film thickness of 5μ-8μ or 0.2 mil, which is equivalent to 1600-1900 mg per square foot. (Slide #3)

Outstanding corrosion resistance is provided by a combination of protective mechanisms. (Slide #4) First, the large number of laminated zinc platelets provides good barrier protection due to the critical pathway required for water and oxygen to reach the substrate surface. Second, the chromium +6 in the coating solution ensures that all the zinc platelets and the substrate surface are passivated. Thus, unlike zinc or cadmium plating, which is given only a dichromate surface treatment, DACROMET®320 has through-film passivation. Finally, the zinc in the coating, which is free of any organic polymer, will provide cathodic protection of the basis metal. It is then this combination of protective mechanisms,barrier protection, Cr passivation and cathodic protection, that provides such outstanding corrosion resistance.

Application.

Now that you know what DACROMET®320 is and how it protects, let me explain briefly how it is applied. There are two basic methods of application.

First, there is the dip-spin process which is designed to apply the DACROMET®320 to bulk fasteners such as nuts, bolts, clips, etc. It consists of three basic steps -- cleaning, coating and baking.

Like with all other metal finishing processes, cleaning is of fundamental importance. With the DACROMET®320 process, we are discouraging the use of acid pickling. We currently require our Licensees to use vapor degreasing or alkaline degreasing to remove normal oils and soils. Dry honing is recommended to remove mill scales, etc.

On this slide showing the dip-spin process you will note several cleaning options. (Slide #5) What is best is determined by the typical product mix to be coated and personal preference. Basically, alkaline spray washing is used to remove the oils. Loose heat-treat scale can be removed by vibratory cleaning with preformed aluminum oxide media, or by dry honing with 120 mesh glass beads. The latter method is very effective for cleaning a wide variety of parts, especially threaded fasteners.

Following the cleaning, the parts are rinsed and dried. Drying is required to avoid dilution of the aqueous DACROMET®320 and because the surface tension of the rinse water and DACROMET®320 are different, which can result in a non-uniform coating.

The clean, dry substrate is then metered into coating baskets for application of the DACROMET®320. Conventional dip-spin coaters are used for this job.

The baskets containing the parts are simply immersed in the DACROMET®320 and then raised above the liquid level and spun to remove the excess coating. No critical residence time is required.

The coating weight is regulated by controlling the DACROMET® 320 viscosity and the coating basket r.p.m.

The coated parts are then discharged into the first conveyorized oven and the metal temperature is raised to about 200°C to set the coating and render it water insoluble. The parts are then cooled, using ducted air, and the second coat of DACROMET®320 is applied.

The second coat is necessary to cover contact or nesting marks caused by part touching part as in any immersion process.

The final bake is to a metal temperature of 300°C to completely cure both coats of DACROMET®320. The time-to-temperature is determined by part mass and oven efficiency. The time at temperature is typically 3-10 minutes.

The second application method, called the dip-drain process, consists of the same steps of cleaning, coating and baking. (Slide #6) However, this method is designed to apply DACROMET®320 to parts which are too large to treat in a coating basket. In this process, the parts are individually hung on an overhead conveyor and transported through a dip tank and oven. Only one heavy coat of DACROMET®320 is required since there is no contact between parts.

If acid cleaning is avoided, both these application methods are free of hydrogen embrittlement and pollution. There is no electrolysis, no acids and no post rinses.

Competitive Coatings

Before discussing the advantages of the DACROMET®320 coating per se, let me briefly review some of the competitive coatings for later comparison. (Slide #7)

You are all familiar with phosphate and oil - a good and relatively inexpensive coating for mild corrosion resistance. The problem with this system is that, prior to end-use application of the coated parts, you end up with either too much oil or not enough. With not enough oil, there is little or no corrosion protection, and with too much oil you have the problem of the oil running out of the containers.

Phosphate and paint can provide fairly good corrosion protection at a medium price. It is used rather extensively on spring steel fasteners. Its biggest problem is that the paint polymer freezes up bolt-washer assemblies, etc. Phosphate and paint are also sensitive to higher temperatures and many solvents.

Mechanical peen plate is a newer coating in the marketplace. At higher coating thicknesses, it can provide fairly good corrosion protection. Its biggest claim to fame is that it eliminates most of the hydrogen embrittlement problem because the zinc or zinc alloy coating is physically peened on by glass beads. Its big disadvantage is simply that it is largely limited by part configuration. If the glass beads can't get into a hidden area, then that area doesn't get coated.

Galvanizing is still widely used on small stampings. It's rather inexpensive, but provides only limited protection, particularly in a salt environment. Usually some post treatment, such as a dichromate or phosphate and paint, is required to obtain good corrosion resistance.

The most common of protective coatings, certainly in the automotive market, are zinc and cadmium plating. The corrosion resistance will vary from poor to very good, depending on the coating thickness and quality. Price will also vary. The biggest problems with both of these platings is pollution and hydrogen embrittlement. (Slide #8)

In summary, all of these competitive coatings have at least one major advantage, but they also have one or more major disadvantages.

Advantages of DACROMET®320

Now, let's go back and look at DACROMET®320. This slide shows an array of untested DACROTIZED® parts, some of which are currently being coated for automotive end use in the United States (coil spring and single-thread spring steel nuts). (Slide #9)

This slide shows a similar array of DACROTIZED® parts after exposure to 500 hours salt spray (ASTM B-117 5% salt fog). (Slide #10) You can see that the DACROMET®320 coating provides excellent salt spray resistance. There is no red rust and very little white corrosion.

In addition to accelerated salt spray testing, let's look at some other test results.

On this slide you see both zinc plated and DACROTIZED® bolts after one year's weather exposure at Kure Beach, North Carolina, a marine environment. (Slide #11)

The next slide shows the results of an independent study conducted by Standard Pressed Steel Corp. 75-T6 Aluminum alloy was drilled to accept 1/4 inch bolts coated with Cadmium and Zinc Electroplating and DACROMET 320. The entire assembly was subjected to 1000 hours of testing in salt spray (5%). The purpose of the test was to determine the amount of dissimilar metal corrosion between the coated bolts and bare aluminum. Note how little galvanic action has occured in the area where the DACROTIZED bolt was fastened.

In addition to providing outstanding corrosion resistance, DACROMET 320 is resistant to solvents, gasoline, brake fluids, and sustained temperatures of up to 300°C. DACROMET 320 also provides a good base for both conventional paints or electrodeposited paints with no additional post treatment. (Slide #13)

Potential

Looking to the future, we see DACROMET 320 being applied to whole assemblies by the dip-drain method.

For example, an automobile door latch assembly containing five springs, a number of moving cams and levers, is usually assembled after the individual parts have been coated; often with different coatings. (Slide #14) With DACROMET 320, the latch could be assembled first and then coated, eliminating costly time-consuming individual treatments.

Because DACROMET 320 is essentially an inorganic coating after baking, there is no organic polymer to interfere with the free movement of assembly parts after coating. Large, heavy parts can also be coated by immersion in dip tanks while suspended from overhead conveyors.

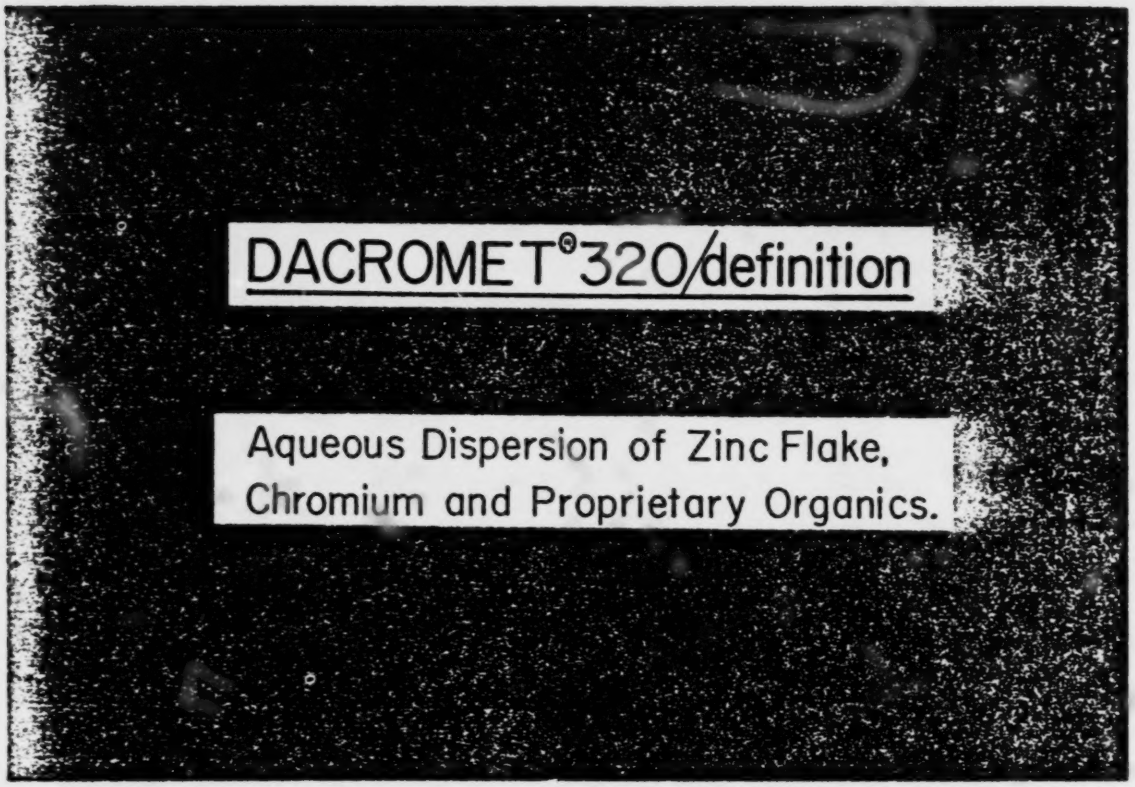
Marketing

The DACROMET 320 process is licensed in the United States by Diamond Shamrock and in Europe and Japan by its Joint Venture Companies, Dacral, S. A. and Nippon Dacro Shamrock Co., Ltd., respectively. The principal target area so far is the one of automotive fasteners because of its extremely high potential. However, the Metal Coatings Division is making a concerted sales effort to penetrate the appliance, building, marine and military market.

To date, General Motors, Chevrolet, Bendix, Delco, Chrysler, Ford (interim), Holly Carburetor, Nissan and Toyota have issued specifications for DACROMET 320. In the appliance industry, General Electric has specified DACROMET 320. A Federal specification was recently issued for use of our coating on nails, staples, brads, and spikes. Before the end of 1977 we hope to have published a tri-service military specification. Further specifications will be written within the coming months. (Slide #15)

In conclusion, DACROMET 320 will not solve all of the metal finishing problems, but it does offer more advantages and greater flexibility to the engineers and designers in metal finishing.

SLIDE NO. 1



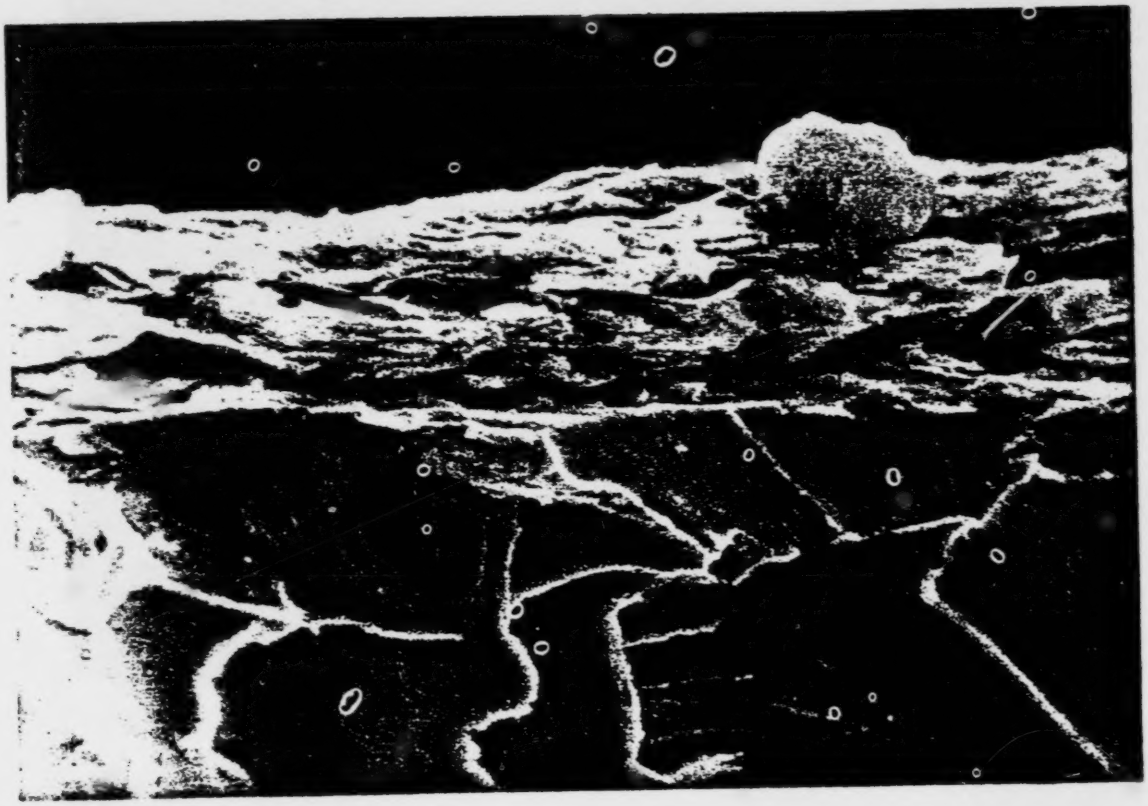
DACROMET® 320/definition

Aqueous Dispersion of Zinc Flake, Chromium and Proprietary Organics.

SLIDE NO. 2 (ZINC FLAKE)

Reproduced from best available copy.

SLIDE NO. 3



SLIDE NO. 4

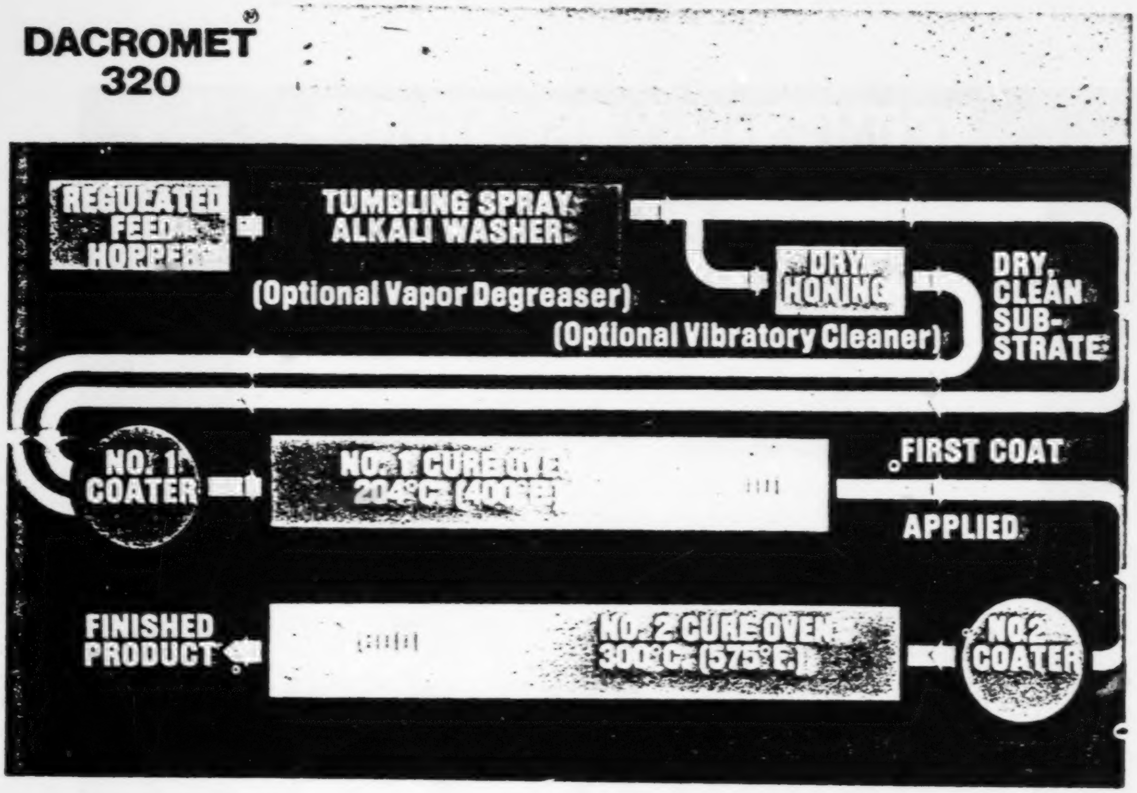
DACROMET®320 EXHIBITS OUTSTANDING CORROSION RESISTANCE UTILIZING A COMBINATION OF 3 PROTECTIVE MECHANISMS.

BARRIER (OVERLAPPING PLATELETS)

CATHODIC ACTION (SACRIFICIAL ZINC)

THROUGH FILM PASSIVATION

SLIDE NO. 5



DACROMET® 320

REGULATED FEED HOPPER

TUMBLING SPRAY ALKALI WASHER

(Optional Vapor Degreaser)

DRY HONING

(Optional Vibratory Cleaner)

DRY, CLEAN SUB-STRATE

NO. 1 COATER

NO. 1 CURE OVEN 204°C (400°F)

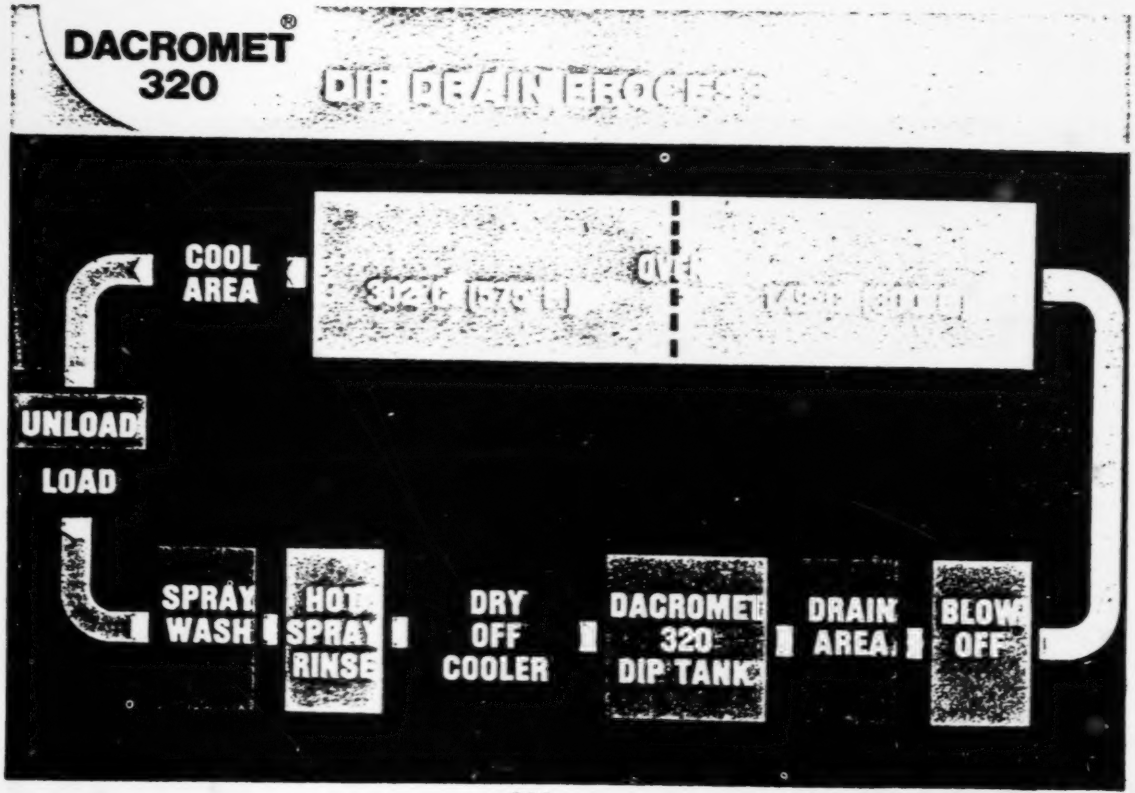
FIRST COAT APPLIED

NO. 2 COATER

NO. 2 CURE OVEN 300°C (575°F)

FINISHED PRODUCT

SLIDE NO. 6



DACROMET® 320

DIP DRAIN PROCESS

COOL AREA

OVEN

302°C (575°F)

[illegible]

UNLOAD

LOAD

SPRAY WASH

HOT SPRAY RINSE

DRY OFF COOLER

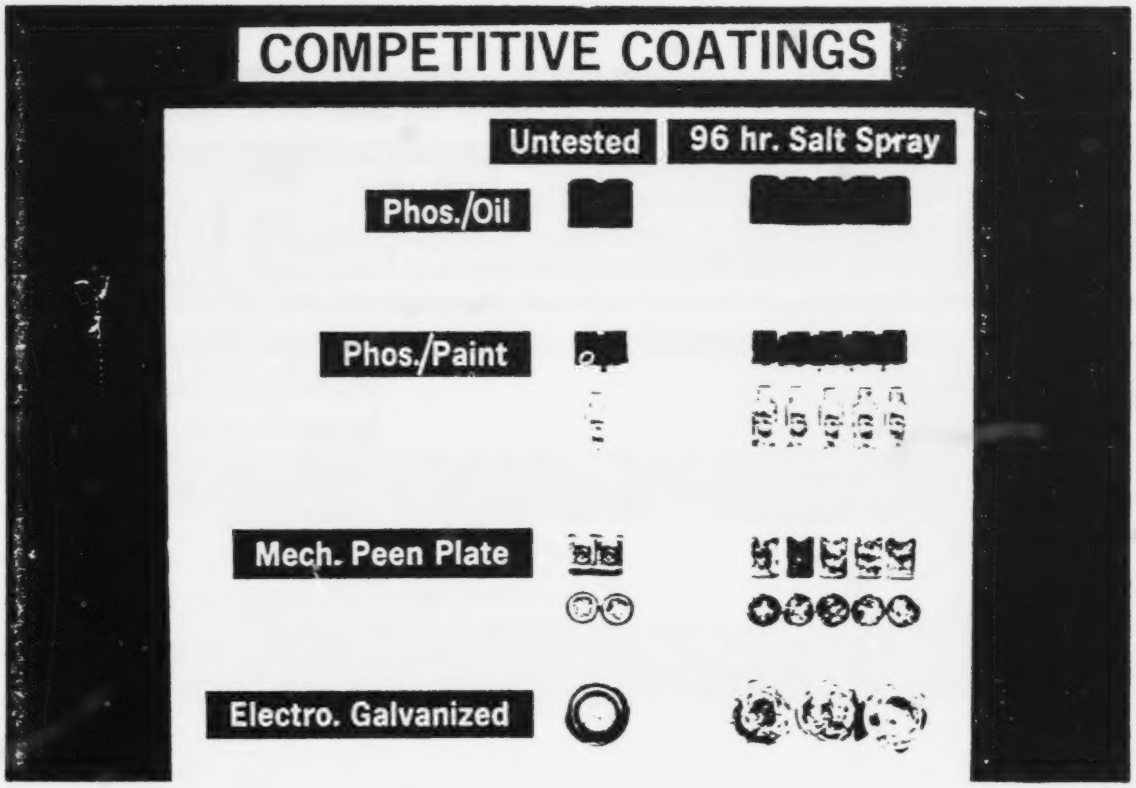
DACROMET 320 DIP TANK

DRAIN AREA

BLOW OFF

Reproduced from best available copy.

SLIDE NO. 7



COMPETITIVE COATINGS

Untested

96 hr. Salt Spray

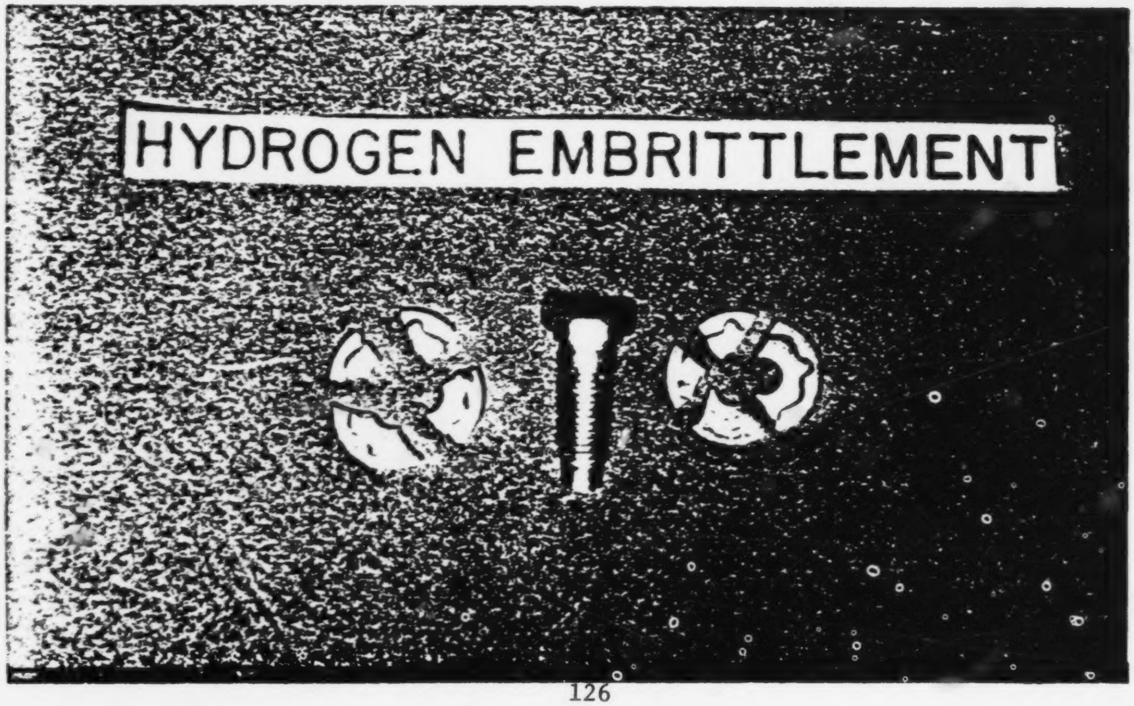
Phos./Oil

Phos./Paint

Mech. Peen Plate

Electro. Galvanized

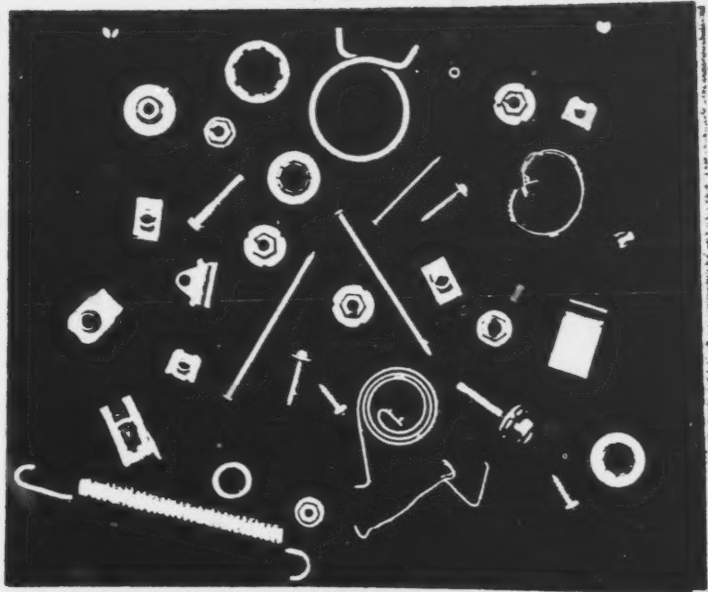
SLIDE NO. 8



HYDROGEN EMBRITTLEMENT

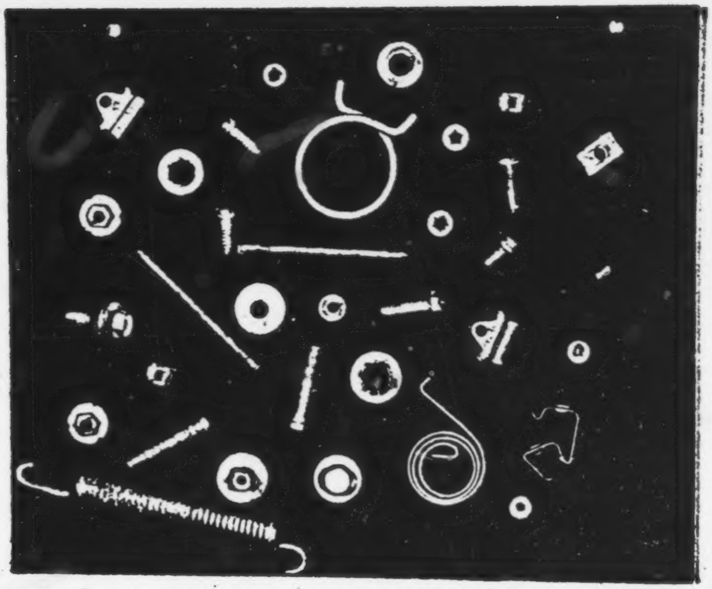
SLIDE NO. 9

DACROMET 320
Untested

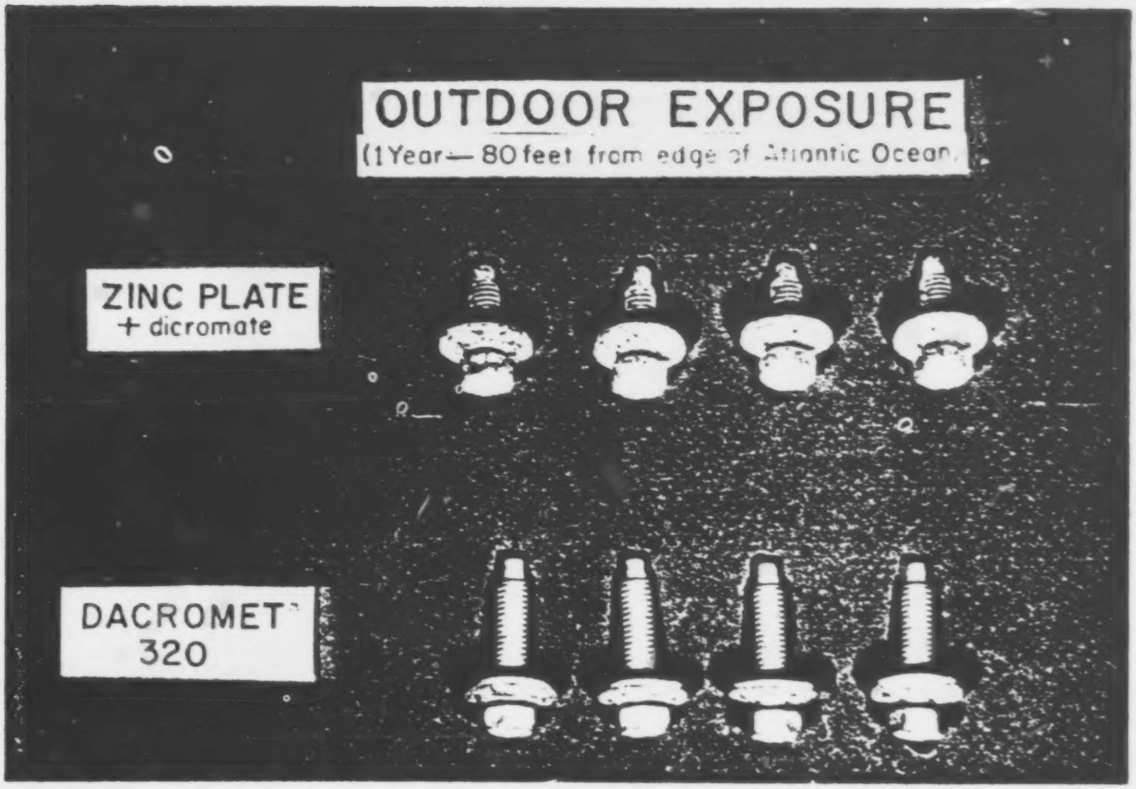


SLIDE NO. 10

DACROMET 320
500 hr. Salt Spray



SLIDE NO. 11



SLIDE NO. 12

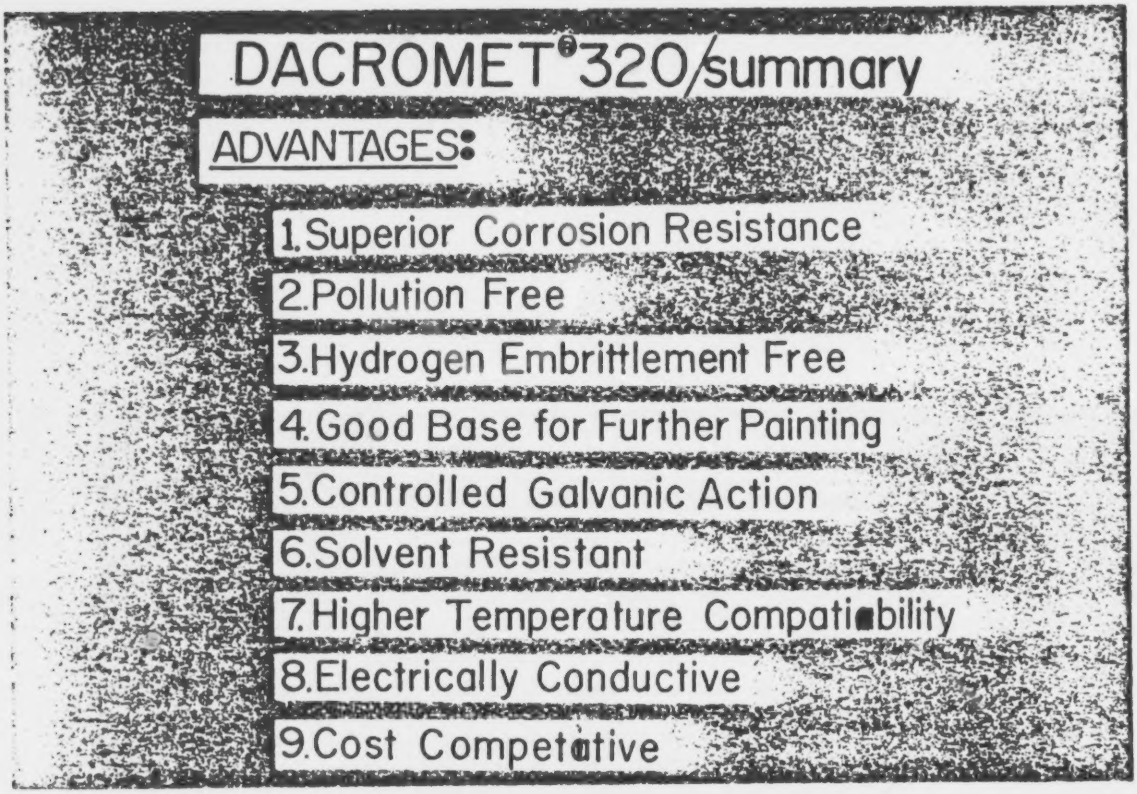
(INDEPENDENT TESTS BY SPS CORP.)

UNAVAILABLE AT TIME

OF

PUBLICATION

SLIDE NO. 13

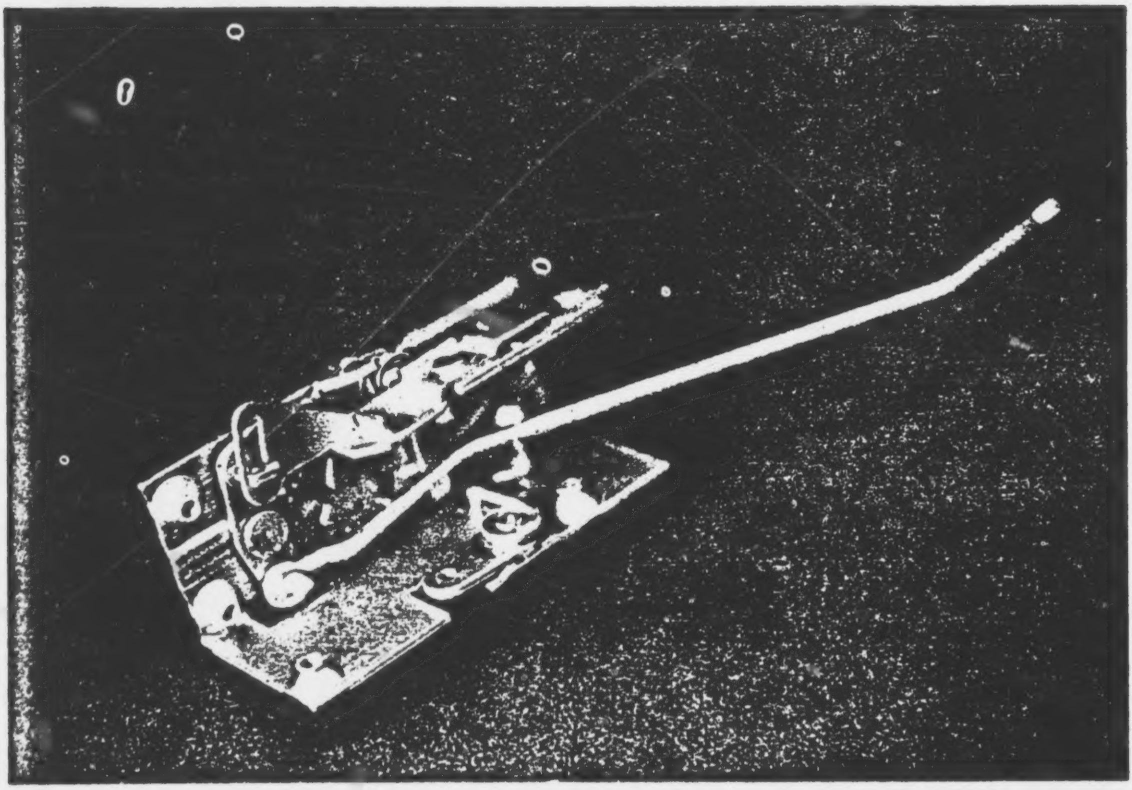


DACROMET® 320/summary

ADVANTAGES:

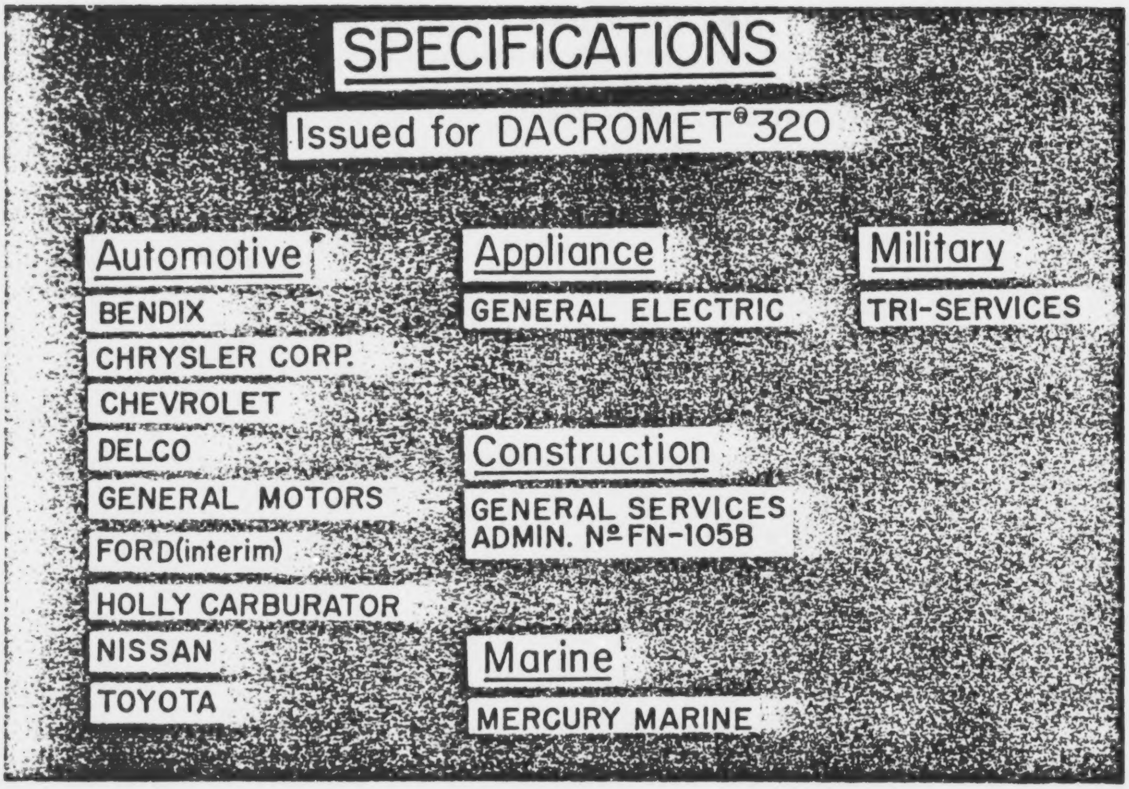
1. Superior Corrosion Resistance
2. Pollution Free
3. Hydrogen Embrittlement Free
4. Good Base for Further Painting
5. Controlled Galvanic Action
6. Solvent Resistant
7. Higher Temperature Compatibility
8. Electrically Conductive
9. Cost Competative

SLIDE NO. 14 (DOOR LATCH ASSEMBLY - DACROTIZED BY DIP-DRAIN)



Reproduced from best available copy.

SLIDE NO. 15



SPECIFICATIONS

Issued for DACROMET® 320

Automotive

BENDIX
CHRYSLER CORP.
CHEVROLET
DELCO
GENERAL MOTORS
FORD(interim)
HOLLY CARBURATOR
NISSAN
TOYOTA

Appliance

GENERAL ELECTRIC

Construction

GENERAL SERVICES
ADMIN. № FN-105B

Marine

MERCURY MARINE

Military

TRI-SERVICES

OUTSTANDING CORROSION PROTECTION WITH ZINC FLAKE IN A WATER-BASED COATING

DISCUSSION PERIOD

MR. WHITE: Martin White, Cadmium Association. I wonder if you could clear up two points on your process.

Your system seems to have a tremendous energy input. You are heating the alkaline cleaner. You are heating the degreasing. You have two heat processes. I'm interested to know how it is costcompetitive for people paying you a license fee on top of that.

MR. KOVELAN : I think one of our disadvantages is that we do have a high temperature cure. As I mentioned, it's about 575 degrees.

I was just talking with our manager of research and development, John deRidder, and we feel that we are costcompetitive with the phosphate oil line.

We are talking about three to ten minutes on that final cure. On the first cure, we are just passing it through to set the Dacromet and render it water-insoluble.

Dacramet 320 can be sold for from nine to ten cents a pound; polyshield goes for about nine or ten cents a pound; phosphate oil, for about three cents a pound; zinc or cadmium, seven to eight cents a pound.

We also know we are selling a license, and I might add at this juncture that one gallon of Dacromet 320 coats about a thousand square feet. This would be 1.3 cents per square foot, I guess, because it costs $13 a gallon, so this is no more expensive than ordinary house paint.

Have I answered your question?

MR. WHITE: A couple of other small points. First of all, you are saying that corrosion resistance is a function of coating weight, but there is also the question of coating uniformity.

I am wondering what happens to the threads of bolts - what is the coating --

MR. KOVELAN : I mentioned that the zinc dichromate was a heavier coating than ours, and we gave you twice the salt spray resistance of the zinc plate for half the coating weight.

I don't think I said the coating weight was a function, because we use only two-tenths or three-tenths of a mil when there are many coatings that use either four-tenths or five-tenths.

MR. WHITE: What I'm trying to get at is how uniform is the coating?

MR. deRIDDER: Dacromet 320 can be compared very much with phosphate paint. We are fighting gravity, and I guess as compared to, say, cad plating where you filled up on the thread pitches, we had just the reciprocal, we tend to build up more in the thread roots and less on the thread pitch. We have been looking at the rayology of the composition very closely, trying to improve that situation, but overall I think the distribution of coating weight is fairly good.

MR. WHITE: I'm interested in the torque characteristics of the coating, because if you have got a flake, you must have a low show of force between the flake. What's your torque characteristics of the coating, because all the fasteners you have shown have been before they have actually been put into position.

MR. deRIDDER: Based on production evaluations by a variety of people using the coating, I would guess it is very comparable to zinc plate; certainly not the lubricity of cadmium.

We have been compared to cadmium, though, on a one-to-one by automotive users using dynamic torque tension equipment with load cells and strip charts. The whole thing, starting, prevailing and plant force can be comparable to cadmium with a friction modifier. Usually we use a very dilute water emulsified wax.

MR. WHITE: Thank you very much.

MR. VAALER: Luther Vaaler, Battelle-Columbus.

All right, perhaps cadmium has some lubricity, or whatever it may have in unique applications. Can't you use this technique with cadmium plate? Why wouldn't it --

MR. KOVELAND: You mean plate over cadmium?

MR. VAALER: No, just use cadmium instead of zinc plate to start with.

MR. KOVELAN: I think again I'm going to have to throw that to John, because John--I'll give you some background.

John has been with this for about 12 or 13 years and he has looked at all the things that have been added to Dacromet 320, including aluminum for the cosmetic effect, but I think John will tell you some of the things that can't be done.

MR. deRIDDER: I checked into this years and years ago, before we ever got involved with zinc, and the initial response was for about $25 a pound they would flake the cadmium, and that dampened our enthusiasm, to say the least.

We have since worked very closely with several of the major metal companies that are in the process or business of making very highly classified dust and flakes and so forth, and cadmium is still almost prohibitive cost-wise as a flake.

We are currently looking at cadmium and other metals blended to find other properties or to prove some of the existing properties.

MR. KOVELAN : I might add that we meet the prevailing torque of the automobile industry, spins five on and five off.

MR. BARTEK: Charlie Bartek, RCA, Cherry Hill, New Jersey.

How do you check for cure of this coating? I am asking you that because at one point in your talk you mentioned the lock assembly that was free of polymer and yet your formulation is based on organic proprietary material. What happens? Does that polymerize in some way?

MR. KOVELAN : Well, it comes out in the stack. We actually destroy all of the polymers and there is no pollution coming out of that stack. There is some glycol, but nothing that is harmful.

MR. BARTEK: What is the mechanism that holds those metal plates together?

MR. KOVELAN: Well, the chromic acid binds the Dacromet 320 to the substrate, and there is some form of oxidation that takes place, and the cure, of course.

Have I answered everything, John, or can you amplify on that?

MR. deRIDDER: Briefly, I wish we knew what the structure was. All we can tell you is that it is some type of chromium matrix with the surface iron and between the zinc flakes. We have a lot of the parts of that puzzle, but not the whole thing.

The chromium is the key binding agent. The organics are shortchanged and completely destroyed. Essentially there is nothing left, maybe a little carbon residue, at best, but really nothing in the way of an organic.

Alternative Materials and Processes

Session II

Tuesday Afternoon 3:45

A PRACTICAL WET IMPACT ALTERNATIVE TO CADMIUM ELECTROPLATING

Lester Coch
Waldes Kohinoor, Inc.
Tru-Plate Division
Long Island City, New York 11101

An improved system for coating base metal parts with co-deposits of zinc, cadmium and tin and cadmium-tin by wet impact plating: The several solutions used in cleaning or otherwise preparing the work, in plating it and rinsing it, are individually segregated after use and re-used in consecutive plating cycles; chemical and metal components fed into the process are conserved instead of being discarded after each plating cycle. No effluent is discharged into sewers. Fresh water use is about 1 volume of water for 25 volumes of parts to be plated. Pollutants are removed as a concentrated slurry.

Coated part corrosion resistance is comparable to cadmium plating for most environments. Parts with Rockwells as high as Rc 55, coated by this process, are always free of hydrogen embrittlement; no energy-consuming stress relief is required after plating. Process is in line with environmental goals of 1) conservation of all materials used, especially water, and 2) no outfall of liquid effluent into the ground via sewer or other conduit. The process is lower cost than cadmium electroplating in most cases.

A PRACTICAL WET IMPACT ALTERNATIVE TO CADMIUM ELECTROPLATING

LESTER COCH
WALDES KOHINOOR, INC.
47-16 AUSTEL PLACE
LONG ISLAND CITY, NEW YORK 11101

Cadmium electroplating, the venerable and excellent standard of corrosion resistance spanning the working lifetime of most of today's corrosion resistance specialists, is truly a carry-over of a less sophisticated age. In today's sharpened climate of expanding demand, limited resources, sensitivity to potential ecological hazards, and heightened competition, the old standby no longer measures up in many ways to current demands and new ways must be found. In finding these new paths, we must never forget that the primary purpose of corrosion protection is just that, and that cadmium electroplating survived all rigors of the marketplace for many years because it was cost-effective in terms of marketplace quality requirements.

We, at Waldes, were among "the early birds" in abandoning electroplating of all coatings, including cadmium. Many of the parts we manufacture are stamped annular springs with minimum virtually square sections of .025" and .035", hardened to Rc 55, and expanded diametrically in use over 10%. Obviously, hydrogen embrittlement was and is a source of real concern to our engineers, and efforts to relieve it by heat treating procedures after electroplating were unreliable at best.

We replaced our zinc and cadmium electroplating with mechanical plating. We started with a purchased system and chemistry: Gradually over the intervening 15 years since that tentative start, we have evolved our own systems, including methods, machinery and chemistry which have been responsive to the changing environmental climate. It is this system, and our new concepts (both in using old materials and new approaches) which form our recommended methods for replacing cadmium electroplating.

First, we will describe in some detail a new system of wet impact plating in which there is no liquid effluent outflow into a sewer. All liquids and the materials they contain are used again and again. Rectification of liquids when required, is done as a part of the machine function, and waste products are removed as a slurry. Water consumption is about 5% of that required by most conventional mechanical plating.

Second, using this new self-contained eccosystem of impact plating, we will show how discreet layers of metals can be used as coatings to engineer protective coatings to meet requirements of corrosion protection, lubricity, etc., with no materials, toxic or non-toxic, being discharged into the environment. Further, we will show how virtually any desired degree of corrosion protection can be achieved by the peculiar ability of this process to achieve any desired degree of thickness.

Third, we will document the corrosion resistance of the coatings by salt spray testing of parts, both unmounted and mounted in a simulated use condition in which plated retaining rings will retain aluminum bushings mounted on various stainless steel shafts. Test results will also be shown as conducted in the harsh real-life conditions of seaside south Florida.

Fourth, we will demonstrate with our test samples that thin metal stampings with fragile minimum sections, heat treated to Rockwell C 55, can be safely plated by our system and heavily stressed in application with no fear of failures due to embrittlement or stress corrosion.

Fifth, we will show by comparative dollar figures that our proposed coating, applied by conventional mechanical plating techniques with our recommended chemistry, compares favorably with the economics of cadmium electroplating. This coating, when applied with our recommended Pollex anti-pollution system, not only compares favorably with cadmium electroplating in the narrower sense of dollars but, more importantly, in the larger sense of much lower water and energy consumption.

Summing up, we will present a plating program responsive to the demands of 1977 for non-toxic coatings of a balanced quality previously obtainable only with cadmium, low in water and energy consumption, free of the traumatic failures often associated with electroplating, with economics which compare favorably with cadmium electroplating, and which has no effluents to even minimally contaminate the watershed.

Mechanical plating is now practiced on a wide-spread commercial scale in two basic forms.

The older of the two forms we call the "interrupted plating method". In this method one or more tanks of cleaner, several rinse tanks and a tank of coppering solution are utilized. One cleaner tank is frequently at an elevated temperature, normally 150°-170°F.

The parts to be plated are placed in a rotating drum of perforate construction (the parts having previously been degreased). The drum is lowered into the cleaner and rotated for several minutes until the cleaning operation is satisfactorily performed. The rotating drum is then lifted from the cleaner tank and lowered into one or more rinse tanks, where it is again rotated briefly. The drum is then taken from the rinse tank and lowered into a copper tank, where the parts receive their copper-flash treatment, again followed by a rinse.

The parts are then emptied into a rotating mill, normally (but not always) a horizontal plating barrel. Glass beads, water, plating accelerator and powdered metal are added, the door is clamped on and the mill is rotated for approximately 30 minutes, at which time the plating cycle is complete.

The parts are then emptied from the mill, normally into a large hoist pan, which is then taken to a separating station, at which point the parts are rinsed and separated from the glass beads. The expended plating liquid and everything else that was in the mill except for the glass beads and the plated parts are carried along with the rinse water into a sump, holding tank or directly into the sewer. See Figs. 1, 2, 3 below.

CONVENTIONAL (INTERRUPTED) PROCESS FOR MECHANICAL PLATING

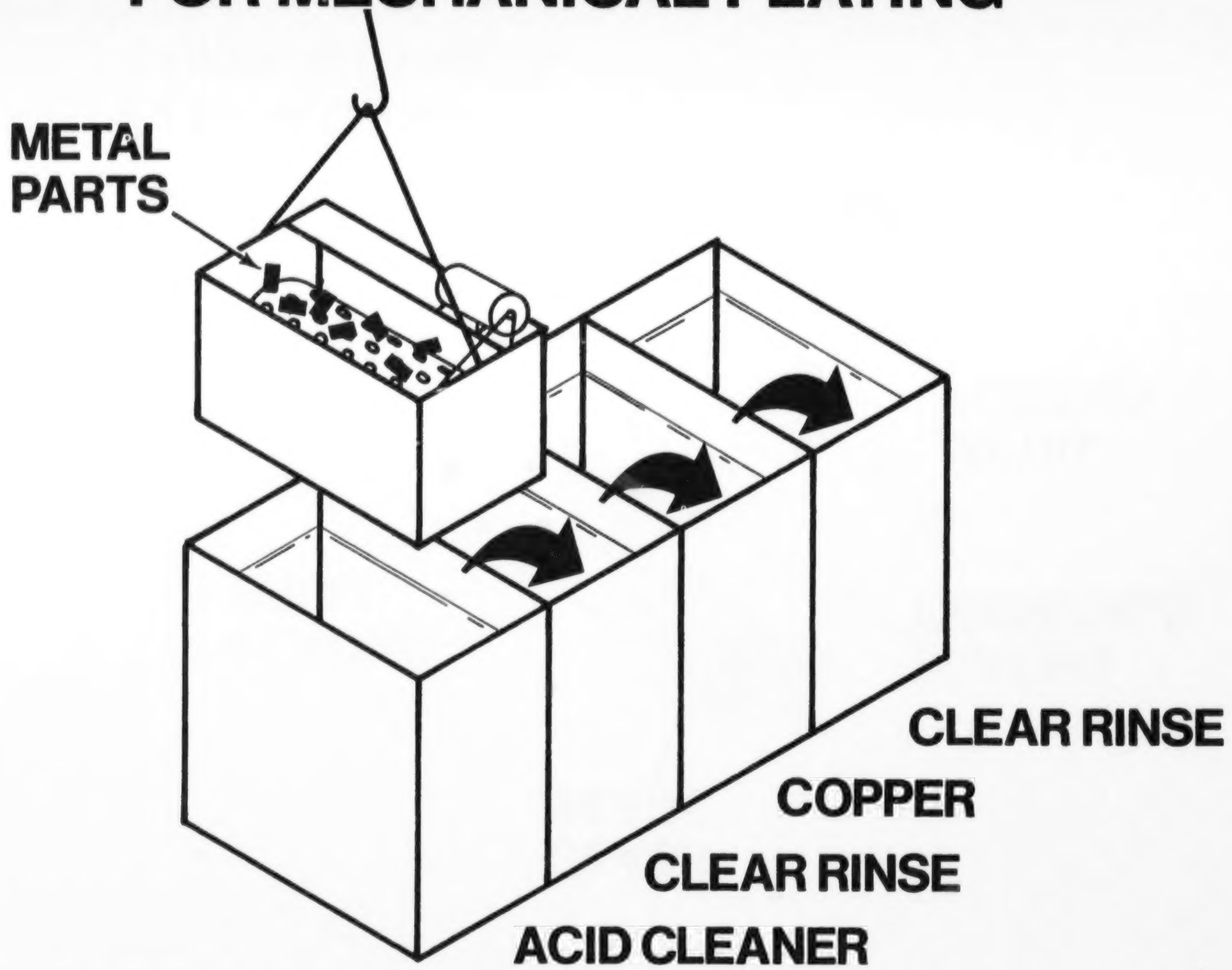


FIG. 1

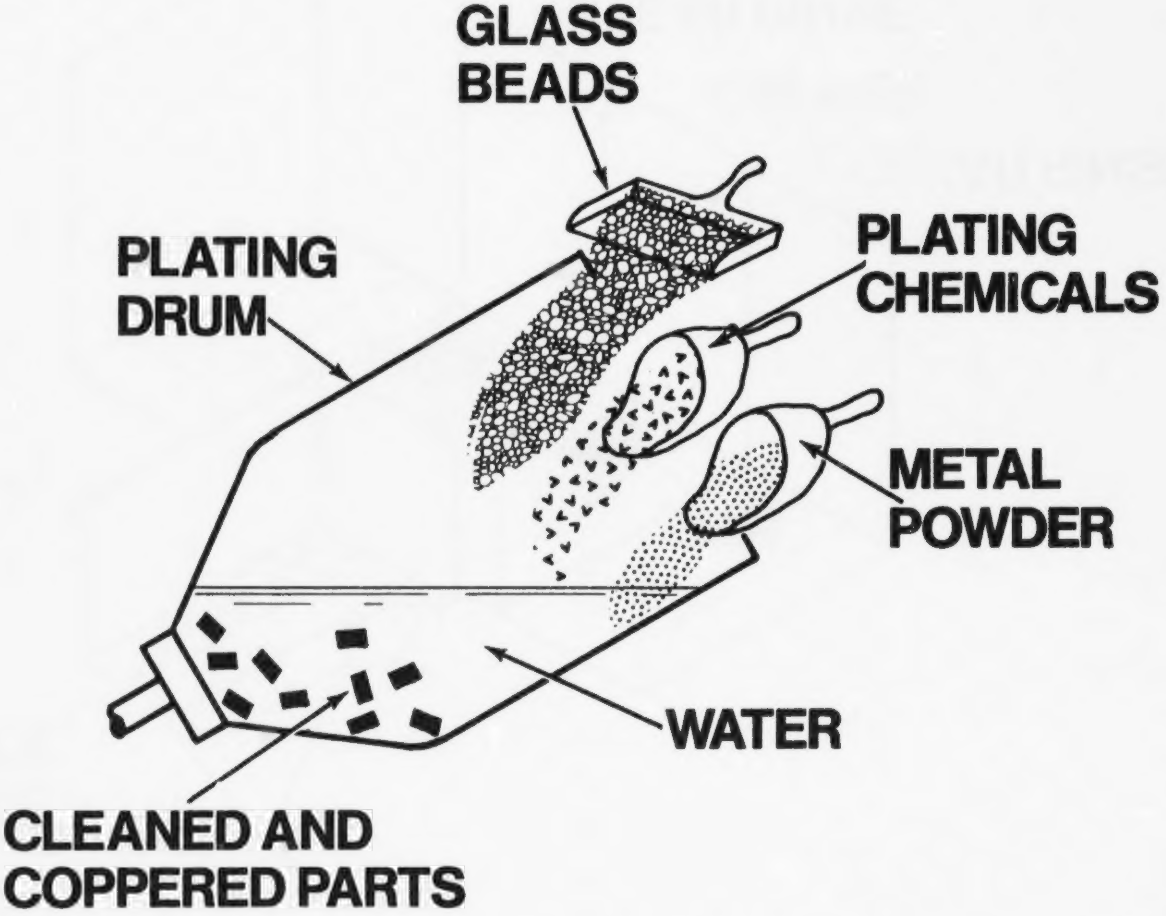

GLASS BEADS
PLATING DRUM
PLATING CHEMICALS
METAL POWDER
WATER
CLEANED AND COPPERED PARTS

FIG. 2

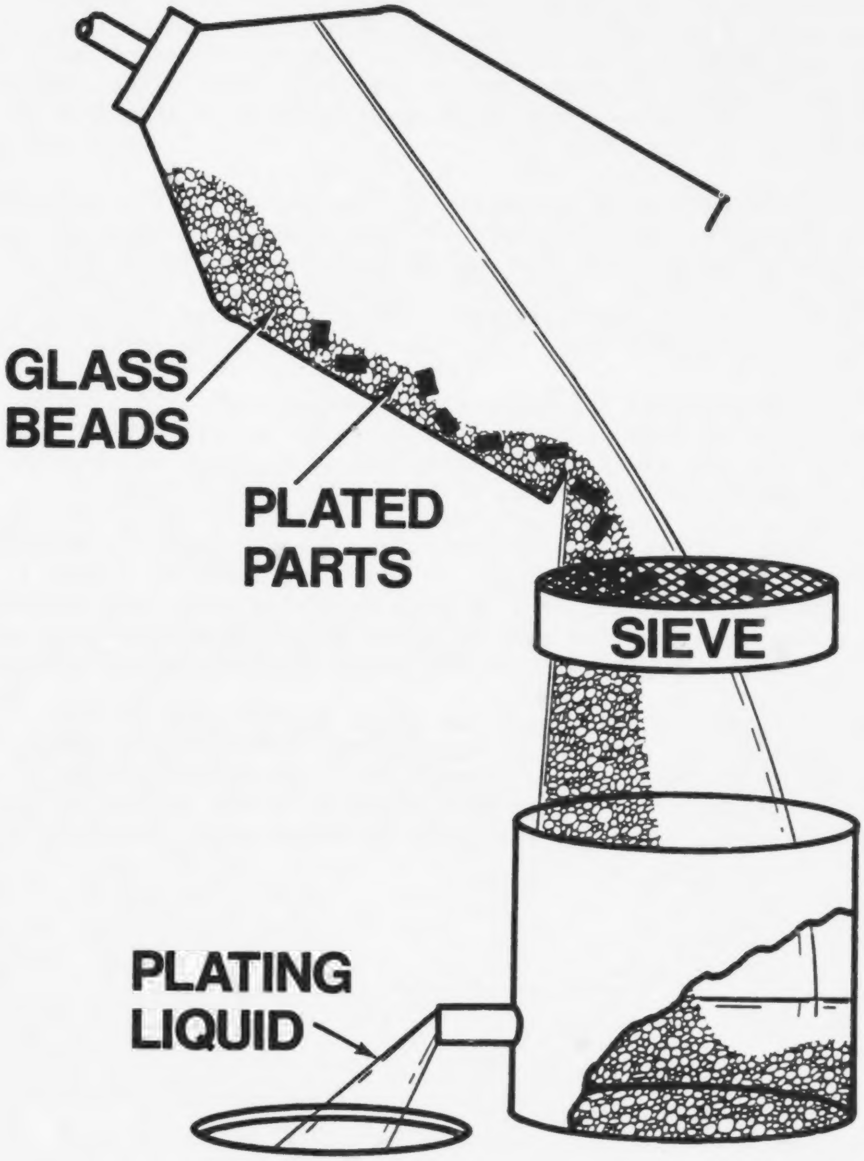


FIG. 3

As generally used, this process depends upon a strong charge of citric acid in the plating accelerator for the driving force of the process and it normally operates in the range of pH 3.0 to 4.5. The process has the advantages of comparatively very low capital expenditure, recovery of the cleaning and coppering fluids and the fact that it tends to bring up a rather bright finish as mechanical plating goes. It has the disadvantages of being rather expensive from the standpoint of material handling and being rather expensive in the expenditure of plating accelerator, compared to more modern systems. Discharge of metal both in solution and in suspension occurs after each plating load; additionally, because of the rather rapid build-up of particulate plating metal on the glass beads, these beads must be stripped in acid frequently with consequent additional discharge of metals in solution.

Many of these disadvantages have been engineered out in various installations, in others platers choose to live with them, but one disadvantage all practitioners of mechanical plating using this system share is the higher cost of chemistry inherent in the system. Despite this real drawback, the system continues to enjoy wide popularity, especially among platers of low-bulk-density parts (parts less than 80 lbs./cubic foot) and tangling parts.

Many plating shops have replaced this interrupted method with an "uninterrupted plating method". In this procedure the degreased parts to be plated are loaded directly into the plating mill, the cleaner is added along with the glass beads and water and the driving force for the plating process comes directly from the acid used in the cleaner, so that the copper solution, the plating accelerator and the powdered metal are added directly in sequence with no interruption or material handling. This process normally operates at pH 1.0 to 1.5 and in general is lower in cost with very much less material handling than the older method. The plating tends to be somewhat coarser on certain part types using this method than when using the interrupted method.

At the conclusion of this plating process the total liquids used in the process are again dumped into the sump or sewer along with the very great volumes of water which are used to separate and rinse the material. When this method is used little in the way of metal adheres to the beads, so that additional stripping, while sometimes required, is quite rare. See Figs. 4, 5, and 6 below.

PLATE-THROUGH (UNINTERRUPTED) PROCESS FOR MECHANICAL PLATING

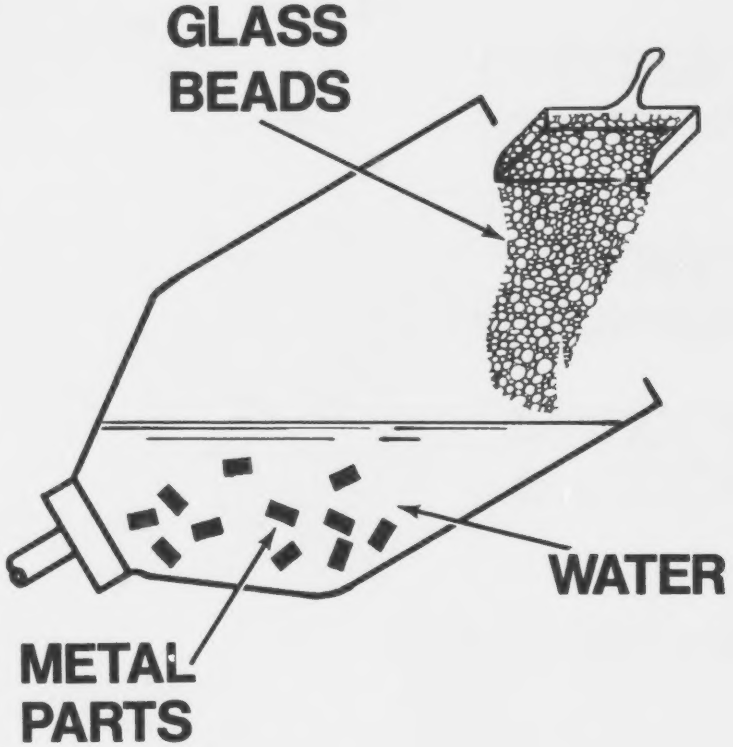


FIG. 4

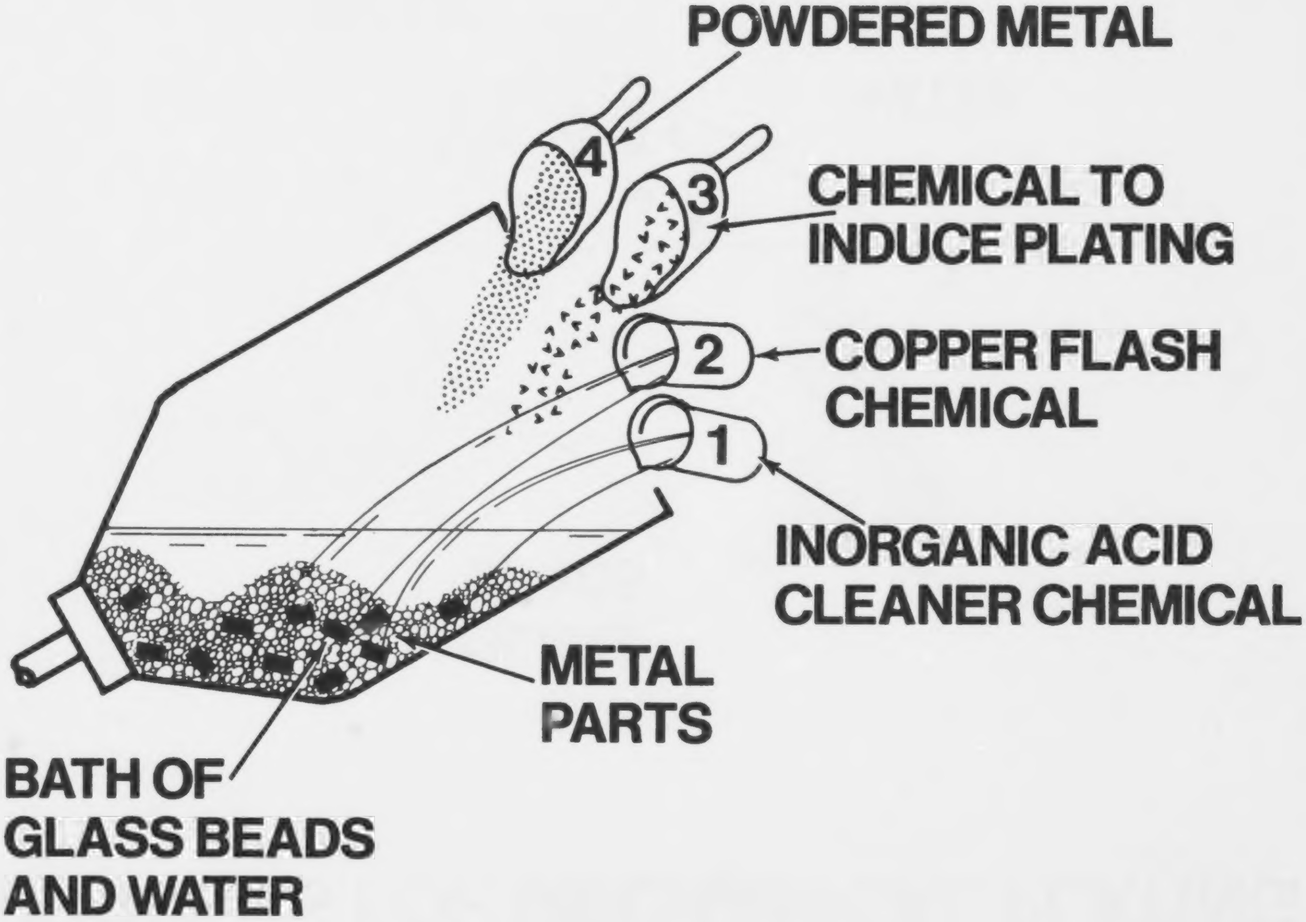

POWDERED METAL
4
3
CHEMICAL TO INDUCE PLATING
2
COPPER FLASH CHEMICAL
1
INORGANIC ACID CLEANER CHEMICAL
METAL PARTS
BATH OF GLASS BEADS AND WATER

FIG. 5

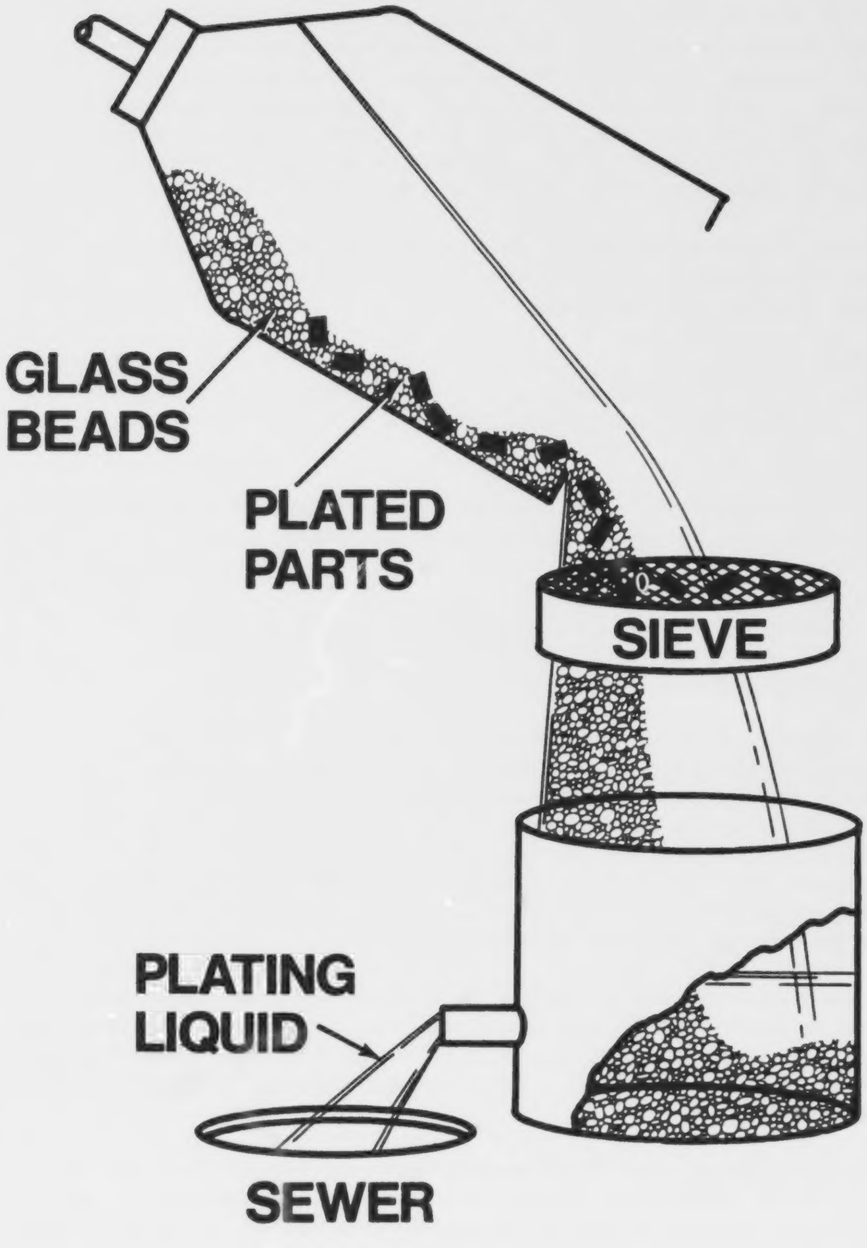


FIG. 6

There are many variances of the above two processes and many combinations, but basically virtually all mechanical plating done in this country today is done by one of these two processes. Both processes are distinguished by the following common characteristics:

1) With wide variations, they both use several volumes of water for each volume of parts plated.

2) Substantial quantities of metal, both in solution and in suspension, are residual after plating and these must either be treated before discharge into the sewer or this discharge will have substantial quantities of metal in suspension and in solution. While the very high water consumption obviously lowers the parts per million of metal content in any given volume of the waste, even this dilution is not sufficient to give reliable low metal concentrations in the process effluent.

3) Both processes are wasteful of chemistry and metal, since both essentially throw away liquids which have large amounts of usable and recoverable material.

A new method by which mechanical plating may be done is the "Waldes Tru-Plate Pollex System". In this system the degreased parts and the glass beads are plated in a semi-automatic tumbling mill. In automatic sequence, the process:

a) Adds a room-temperature cleaning solution, rotates the mill for several minutes, drains the solution off and back into the cleaning solution tank.

b) Adds a coppering solution, rotates the mill for several minutes until the parts are coppered, and then drains the coppering solution back into the copper solution tank.

c) Ends the automatic cycle by adding the plating liquid from the plating accelerator tank. Manually, powdered plating accelerator and powdered metal are added, the mill is rotated until plating is effected. The plating liquid is then drained back into the plating accelerator liquid tank, the parts are then separated from the beads with rinse water which is caught and recycled continuously. Parts are always dried by centrifuge in this process.

This unit is operated with no outlet valve to a sewer or sump connection; none is ever required so far as we now know. Since the process is exothermic, there is some liquid lost by evaporation and by dragout; these losses must be made up by addition of clear water. However, no liquids are discarded into the sewer at any time.

All plating fluids, including the rinse water, are rectified from time to time chemically in their tanks with sludgy materials being removed to an evaporating pan. Waste materials are alternately removed as a thick sludge or dried solid material. See Figs. 7, 8, 9, 10, 11, 12, 13 below.

WALDES TRU-PLATE® NON-POLLUTING SYSTEM FOR MECHANICAL PLATING

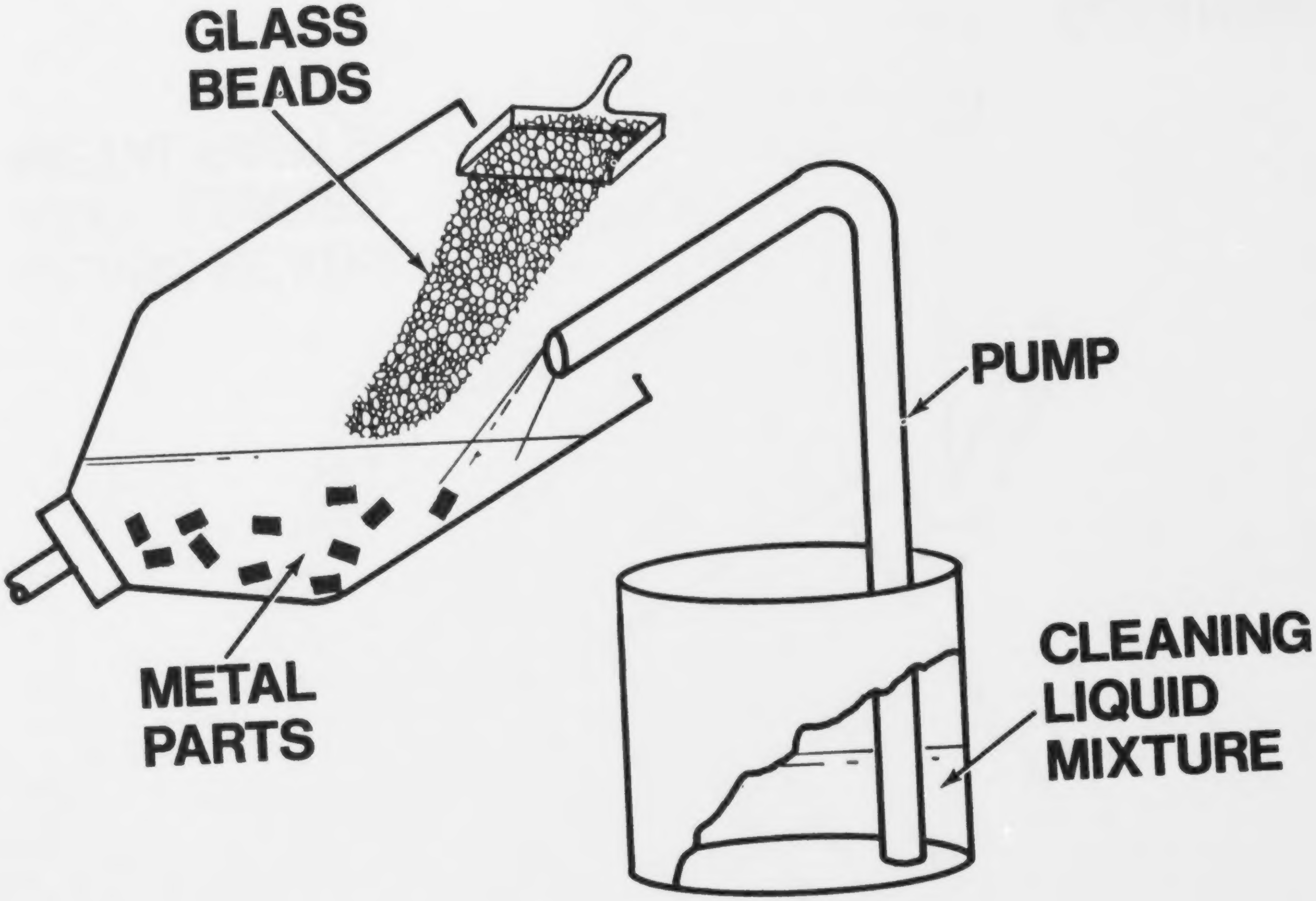


FIG. 7

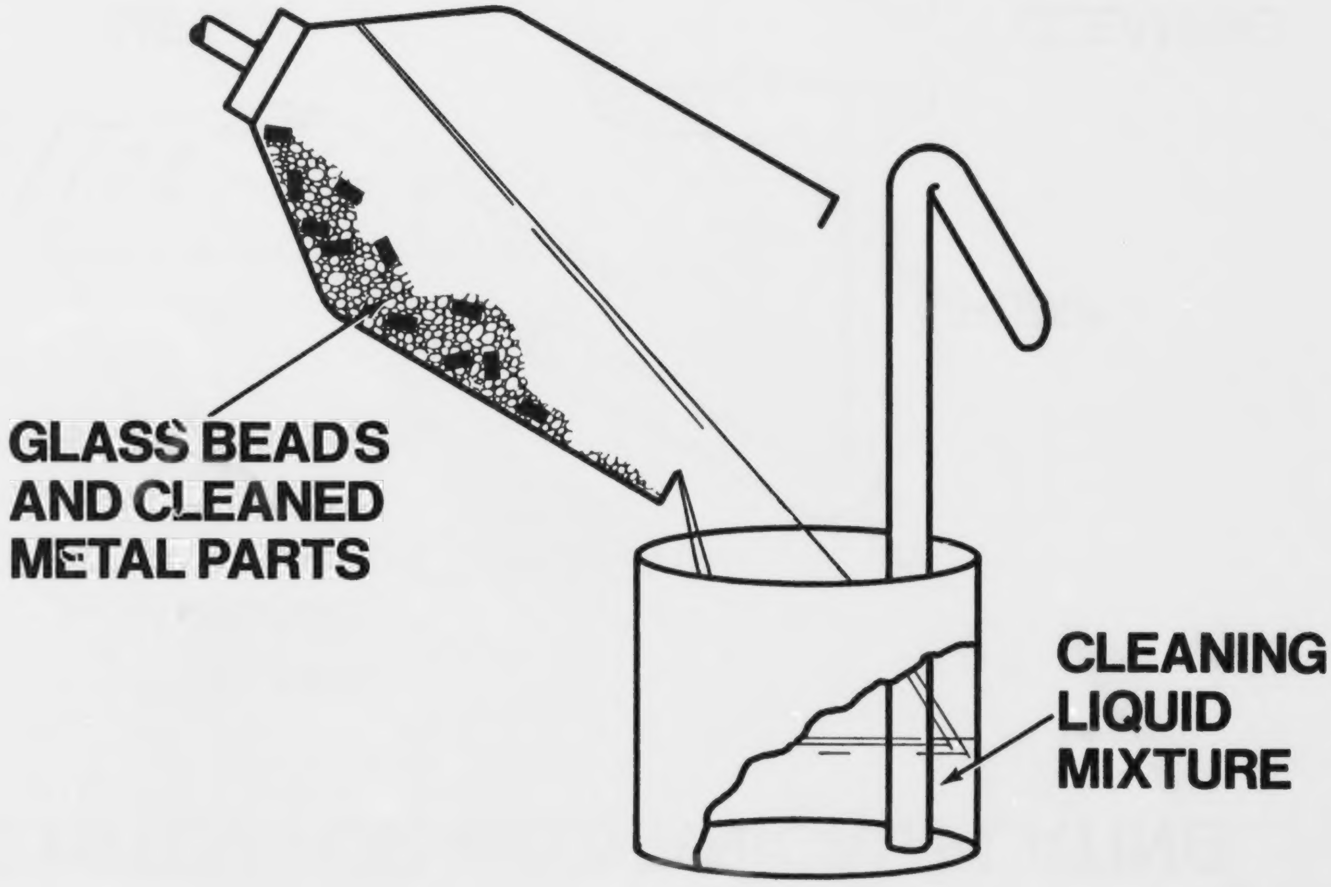

GLASS BEADS
AND CLEANED
METAL PARTS
CLEANING
LIQUID
MIXTURE

FIG. 8

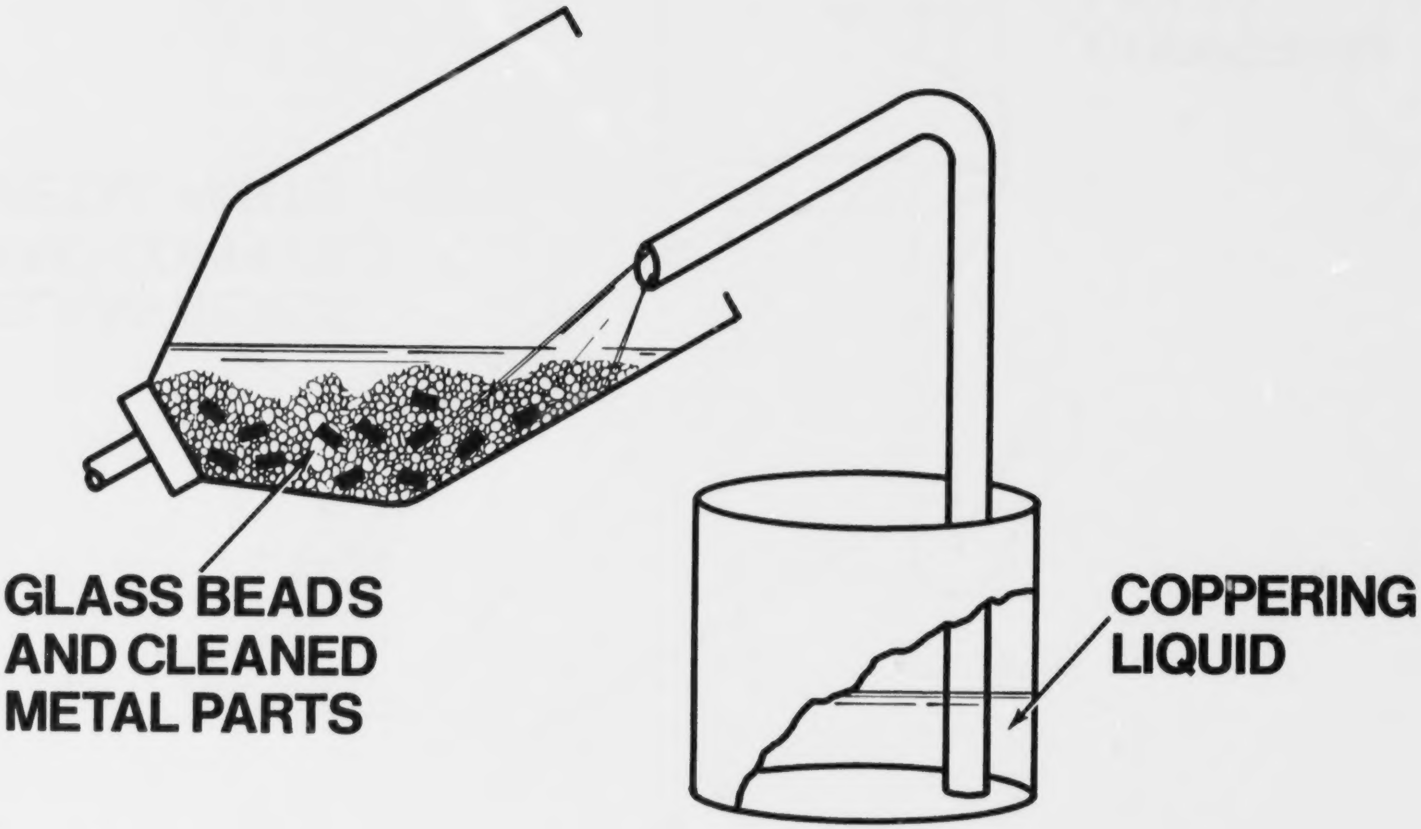


FIG. 9

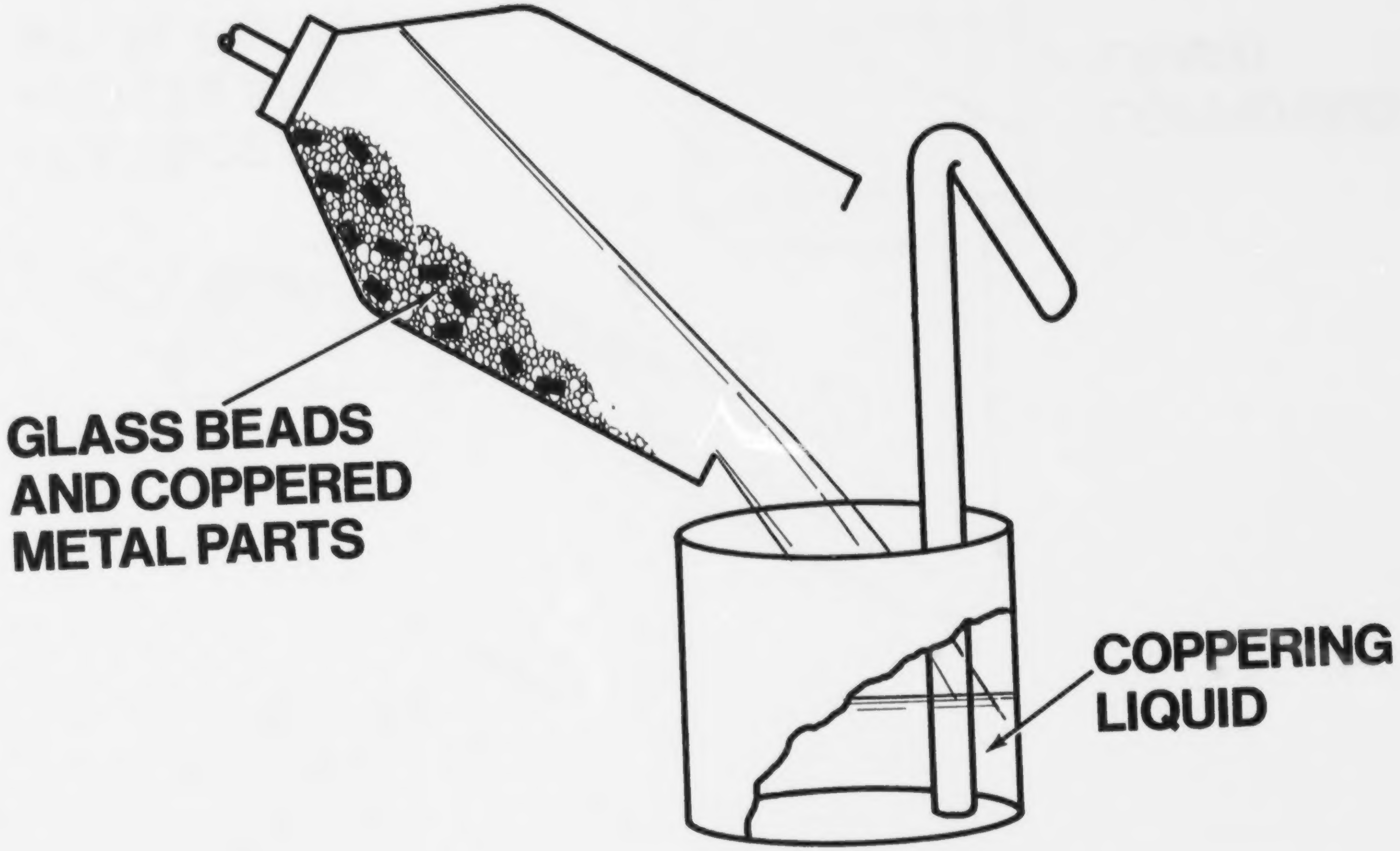


FIG. 10

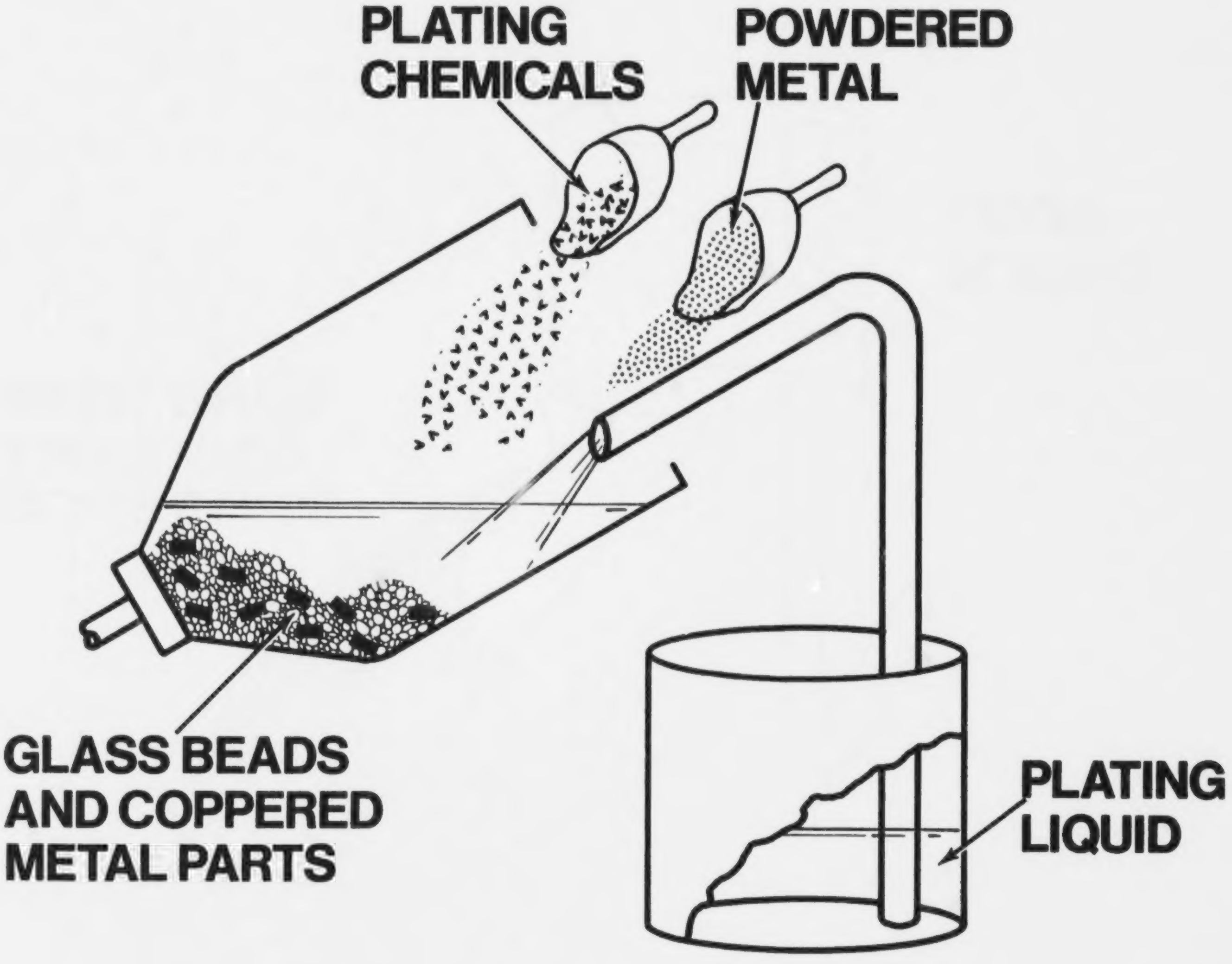

PLATING CHEMICALS
POWDERED METAL
GLASS BEADS AND COPPERED METAL PARTS
PLATING LIQUID

FIG. 11

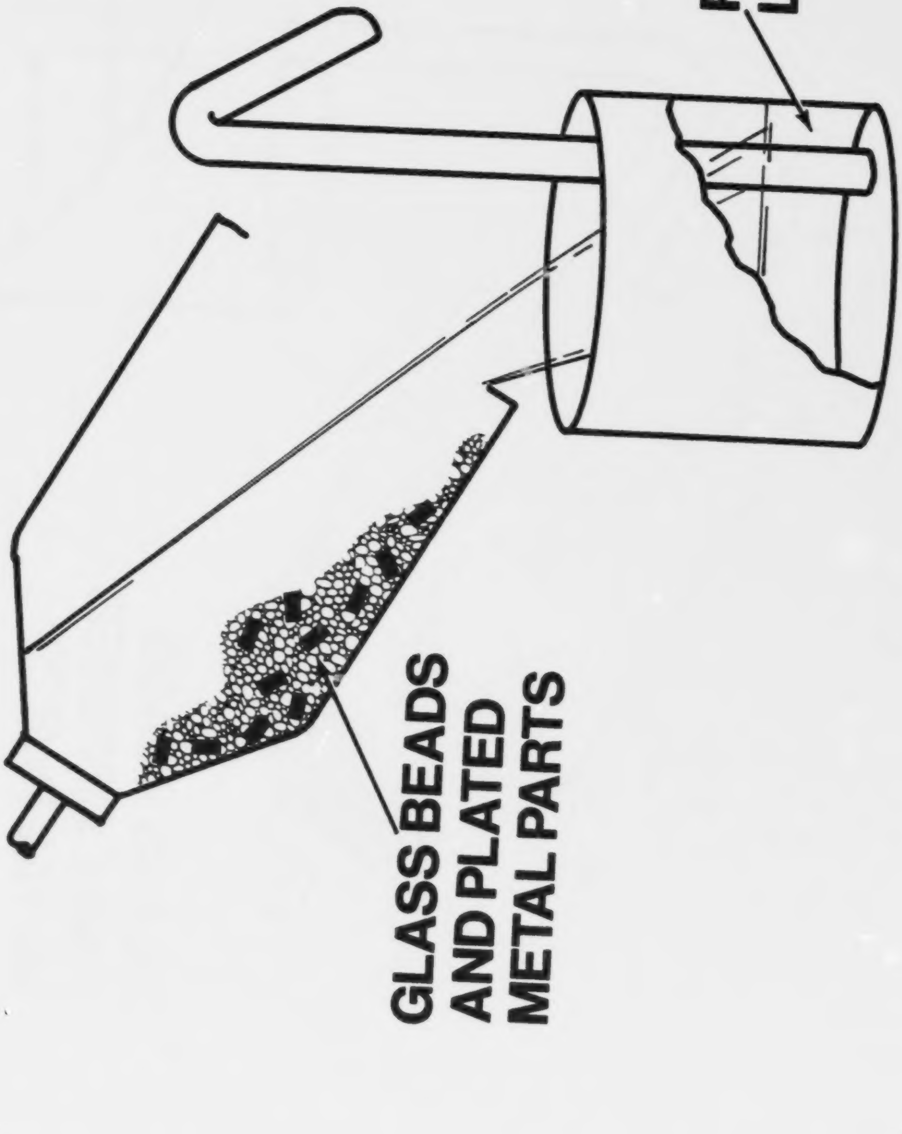


FIG. 12

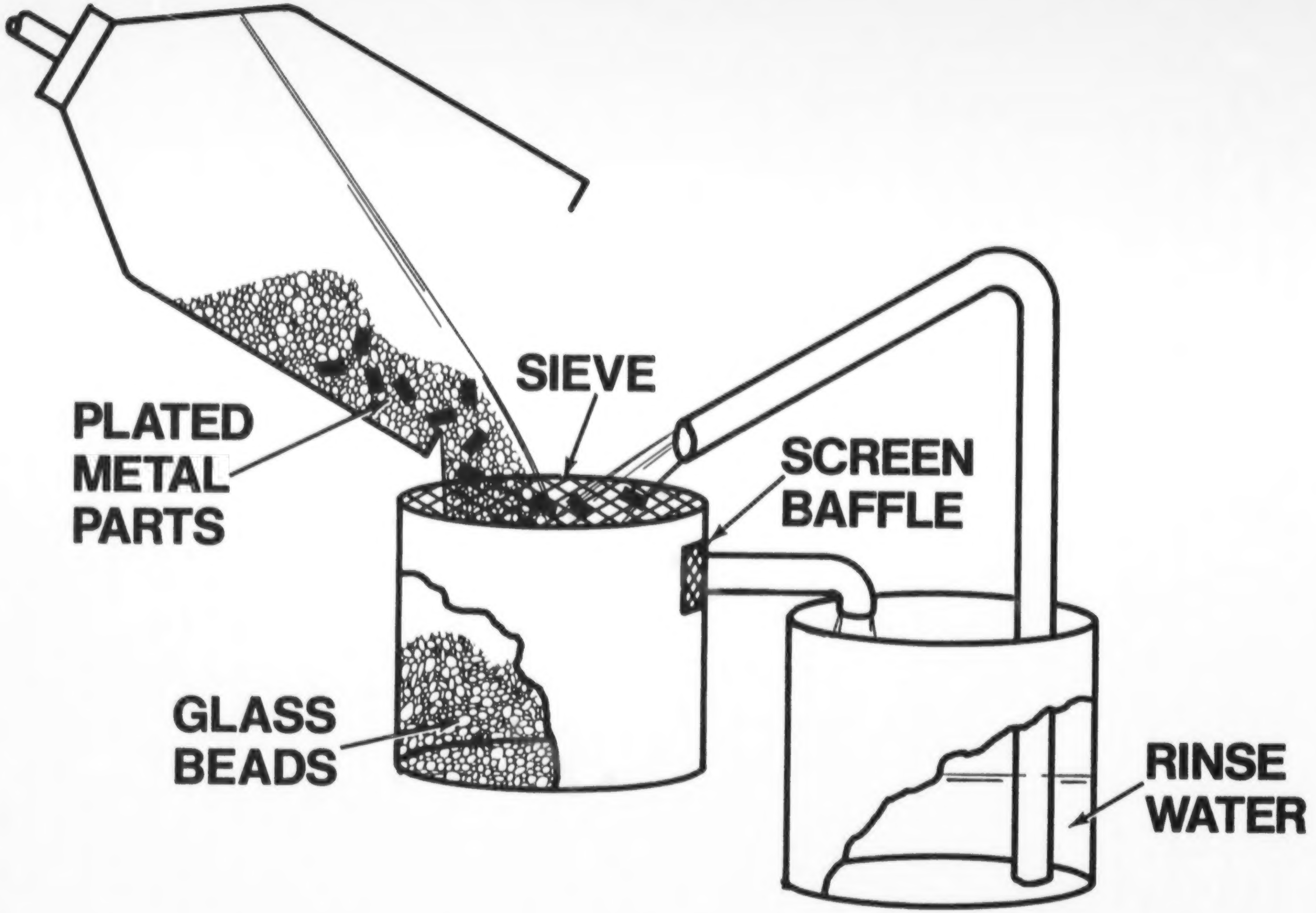

PLATED
METAL
PARTS
SIEVE
SCREEN
BAFFLE
GLASS
BEADS
RINSE
WATER

FIG. 13

Expenditures for chemistry in this process are only about 60% of the expenditures of today's lowest cost method and much valuable material is reused rather than ending up as a noxious effluent to be removed by the producer or the community or to foul the watershed. Water consumption is approximately 1 volume of water for each 25 volumes of plating and the nature of the machine and the process is such that it lends itself well to partial automation, thereby making larger machine assignments possible.

It seems clear that the development of the "closed loop" Pollex system of mechanical plating, from which no effluent is discharged into the watershed, is a giant step forward in the protection of our streams and rivers. It is also clear that its unique economies in the conservation of energy, water, metal and chemistry is in tune with the times and opens new vistas to the corrosion protection engineer. It is an idea whose time has come!

Market analysis of specific coating function requirements by manufacturers presently using cadmium electroplating shows that while all users expect good protection against rust from this coating, other characteristics frequently have great weight in their choice of cadmium electroplating. Foremost among these is lubricity, which may greatly affect the torquing of threaded fasteners, the application and function of spring-type electrical fittings, the insertion of radial-type retaining rings in grooves, etc. Another significant virtue of cadmium is its good protection against white corrosion products. A very important requirement frequently encountered is that it be inert when in contact with various alloys such as aluminum, stainless steel, etc. Proposed alternatives to cadmium electroplating must consider these requirements as well as extended resistance to red corrosion, to truly meet all market requirements, hopefully at no increase in cost.

The simplest and most straightforward alternative possible to cadmium electroplating, which will meet all these requirements and protect the environment against cadmium-bearing effluents as well, is cadmium mechanical plating done according to the Waldes Tru-Plate Pollex system. Since there is no effluent from this process, the requirement that no cadmium enter the watershed is fully met by this plating process. (Since the plating is cadmium, it will have the characteristics of cadmium electroplating and surely meet all requirements. Indeed, mechanical deposition of cadmium offers expanded possibilities in corrosion protection by means of heavier thicknesses of coatings; coatings up to 50µ are practical, as are co-deposits with other metals such as tin.) For the ultimate in corrosion protection, coatings using cadmium have no peer.

We feel that there will be an ongoing requirement for mechanical cadmium plating, done in a non-polluting process in selected plating stations, carefully monitored. But it is clear that the greater the volume of cadmium plating done, the greater the danger of some cadmium entering the eccosystem, perhaps by careless handling of a stripping solution or some "goof" not presently foreseen. But there are many applications existing today which are routinely specified as cadmium electroplating which do not require the supreme rust protection of cadmium but which do require some or all of the other virtues of cadmium.

One way in which less cadmium is used today in mechanical plating is by plating co-deposits as, for example, 50% cadmium, 50% tin. Mechanical plating of co-deposits is done by any of the mechanical plating systems previously described, making each required metal powder addition half cadmium, half tin. The agitation of the mass assures a reasonably uniform distribution of the cadmium and tin in the coating. Since the properties of cadmium and tin are supportive in most cases, the value of the coating in most cases is as good as cadmium alone; in many applications, the coating values are enhanced.

Certainly, this is one way in which the amount of cadmium used can be reduced by half. Unhappily, the cost of tin makes this finish more costly than cadmium alone, adding about one-and-one-half cents per square foot for a 7 micron coating over cadmium alone.

However, since tin worked well in co-deposit with cadmium, we should not overlook the possibility that the use of lower-priced and less toxic zinc will be effective as a co-deposit with tin. Certainly the economic problem will be overcome; the resultant coating will be less expensive than cadmium alone. But it is at this point that we run into a limitation of the melange approach: The properties of the co-deposit are the properties of both the components all through the coatings. The synergism of the cadmium-tin mixture is noticeably absent in the tin-zinc mixture.

Zinc tends to have two basic drawbacks as a replacement for cadmium, even in the cases where protection requirements against rust are moderate: It has poor lubricity, which makes it a less desirable coating for many threaded and other fasteners requiring good lubricity and it has a tendency to form white corrosion products after a comparatively short exposure to many atmospheres. The tin in a zinc-tin co-deposit does assist in giving the coating a greater lubricity than zinc alone, but the resultant lubricity of the zinc-tin combination falls far short of the desired standard for lubricity, that of cadmium plating. Further, in most tests, the tin portion of the coating seems to do little in extending the coating life to white corrosion failure.

Understanding clearly that in the nature of things, there will be some applications for which the tin-zinc co-deposit will be useful, we believe we "have found a better way".

One technique used in mechanical plating is adding the required amount of metal powder in small doses to achieve a smoother, more cohesive finish. For example, a 12 micron thick zinc plating on a part having 1 square foot of surface area per pound of parts requires 9 grams of zinc powder per pound of parts. Good mechanical platers ordinarily apply the metal powder in two equal additions of 4.5 grams per square foot each to the plating barrel at about 15 minute intervals. In effect, they plate two separate layers of zinc with perfect cohesion.

There is, of course, no reason that the separate layers have to be the same metal, or the same thickness or that we could not have several layers rather than two. For example, one practical alternative to a 12 micron co-deposit of tin-zinc might be a 10 micron thick coating of zinc covered by a 2 micron thick coating of tin. That would have the effect of putting the tin "up front" so to speak, where it would certainly improve the lubricity of the product to the equivalent or better of cadmium plating, and exert a benign effect in resisting the formation of white corrosion products.

Such a treatment is, in our opinion, a better treatment than co-depositing tin and zinc and, obviously, uses only 1/3 the tin of the co-deposit on a 13 micron coating, saving about $.04 in metal per square foot at current tin prices. The time per plating run would be extended several minutes, which is a cost adder. There is a more serious criticism of this technique as I have described it; it applies equally to putting on a final layer of tin using powdered metal and to co-depositing tin with zinc. The plating is rather lumpy as a rule; far more so than is common with quality mechanical plating. This is especially noticeable with low bulk density parts (less than 80 lbs./cubic foot) of high surface area. This is caused in part by the coarse particle size of powdered tin.

There is another approach to the same problem that plainly seems tailor-made for mechanical plating. Returning to our previous example of the 12 micron coating, we can take the 2 microns of tin from tin salts. This top layer, put on in a proper chemical ambience over a quality mechanically plated base of zinc, yields the smoothest and most lubricious mechanically plated surface we have ever seen, and one which functions in many key ways as well as or better than the finest cadmium electroplating, particularly with regard to uniformity and ease of torquing threaded fasteners so plated. Costs of the process and materials are competitive with all other mechanical plating approaches to the problem of replacing cadmium electroplating and, in most cases, with cadmium electroplating itself.

The concept of layered plating has additional value in the search for a replacement for cadmium electroplating. Using our effluent-free Pollex process, it is possible to effectively coat parts with, for example, 2.5 microns of zinc as a base, a second layer of 2.5 microns of cadmium and a top layer of 2 microns of tin as previously described. Such a coating retains all of the lubricity values previously described, further improves the corrosion resistance against both white and red corrosion and still is attractive economically.

This zinc-cadmium-tin layered coating has an attractive bonus plus. The nature of mechanical plating is such that a failure in the plating process is almost always caused by one of several possible errors, the effect of which would be clearly visible on the first layer of zinc. Thus, a plater who always used a first layer of zinc, before putting on a layer of cadmium, and who inspected the plating deposition of the zinc layer carefully before putting the cadmium powder in the plating barrel could largely avoid the problem of stripping, since success through the stage of the first layer virtually assures successful completion of the plating. To the extent that cadmium plating is required, the combined practice of using the Waldes Pollex mechanical plating system and the use of a zinc first layer of plating would certainly minimize danger of any entrance of cadmium into the watershed. We feel, however, that the bulk of existing cadmium electroplating can be replaced by a zinc coating with a layer of tin on the surface. This layer of tin will normally be 2.5 microns thick over 5 microns of zinc; Exact tin-top thicknesses specified will always be a function of the end product requirement.

The use of chromates is not always necessary with the tin-top plating described above but it does greatly further enhance the corrosion resistance of the plating. Depending on the thickness of the tin coating, it is frequently not visible and rarely assumes a full yellow chromate color but its use, particularly with coatings of 5 to 7 microns of thickness, assures good corrosion resistance against both red and white corrosion. Clear chromate coating over mechanical plating does not add the corrosion resistance it does to electroplating. To get a significant effect reliably from lot to lot, it is necessary to use a yellow chromate and leach. This is distinctly less of a problem with the tin-top coating, since normal chromating over tin-top plating frequently shows only the mildest tawney coating and leaching where required should not be difficult.

Summing up, we believe that the Waldes Pollex mechanical plating system can deliver several coatings to serve as viable alternates to cadmium electroplating with no danger of polluting the watershed. These are:

1) Cadmium mechanical plating

2) Cadmium co-deposited with tin mechanical plating

3) Layered plating, designed by specific requirements of corrosion resistance and lubricity, in which a base layer of zinc would be covered with a top layer of tin, with an intermediate layer of cadmium as an optional additional possibility where corrosion requirements demanded it. Tin-top plating, which uses only tin and zinc to replace cadmium electroplating, can be made by many existing mechanical plating installations, requiring only a new chemistry and technique.

Setting up a test program by which the virtues of the various platings might be assessed, it is advantageous to work with non-threaded as well as threaded fasteners, since certain key parameters such as hydrogen embrittlement and stress corrosion are far easier to evaluate in a spring-type fastener than a threaded fastener. Obviously, lubricity is best evaluated for most purposes in threaded fasteners.

The spring steel part chosen for our test is a radial type retaining ring of a new and hard-working type. It is made of 1075 steel, .050" thick and designed to work in a groove cut into a half-inch shaft. The basic part is stamped at high speeds in blanking dies and heat-treated to Rockwell C52-55. The part was originally designed for the farm implement industry and is widely used in both automotive and the farm implement industries as a workhorse when extra strength is needed. Loading on these parts is always bi-axial, with static thrust load and frequently some impact in the axial direction, and working stresses in the area of 170,000 P.S.I. in the radial direction to clinch the ring in its groove.

The parts are heat treated isothermally, austenitized at 1500°F in a neutral atmosphere with a dewpoint of 35°F and quenched in violently agitated nitrate-nitrite salts at 540°F for one hour. Normally, plating is done directly after heat treating: however, some lots require a special intervening deburring. The actual distribution of Rockwells shows a mean Rockwell of roughly 54.5, with a low of 53 and a high of 55.5 - a good typical distribution from our isothermal heat treating process. All samples which were Rockwelled were, of course, discarded, since the penetration mark does constitute a notch at these Rockwells.

ROCKWELL "C" DISTRIBUTION
TEST SAMPLES

ROCKWELL "C"

53 - X
 -
54 - XXXXXXXXXXXXXX
 - XXXXXX
55 - XXXXXXXXXX
 - XX

EACH "X" REPRESENTS 3% of Σ

ROCKWELL "C" DISTRIBUTION
TEST SAMPLES

MEAN = 54.44
S.D. = 0.58
N = 50.00
MIN = 53.00
MAX = 55.50
RANGE = 2.50

Tin-top plating samples were prepared by all three mechanical plating methods - the uninterrupted, the interrupted and the Pollex method. Other samples which were prepared, such as tin-zinc mixtures, cadmium, etc., were generally prepared by the uninterrupted method.

Our bitter experience has shown that on these part types, heat-treated to RC 55, there is no combination of electroplating, pre-treatments and post-treatments which will give any real degree of security against hydrogen embrittlement. Thus, the first test requirement in our program is to demonstrate by overtesting that all parts plated by this process are free of embrittlement.

Our normal test for this is to mount the ring in such a way that the stresses in the radial direction are raised to about 200,000 lbs. P.S.I. and hold it at this stress level for 8 hours. No failures are permitted from a 20-piece sample.

For this test, we turned 200 test shafts, each containing 2 grooves of a diameter which raises the working stresses of the rings in the radial direction to 205,000 lbs. P.S.I. The 400 rings so tested, about 20 each from the 20 test lots made, remained on the grooves for various lengths of time from 4 to 14 weeks.

100 of the test shafts were made from 430 stainless, 100 were made from 304 stainless. For each shaft, a bushing of 7076-T6 aluminum was turned so that it was a close fit on the stainless shaft and so that it was retained tightly by the two plated retaining rings.

It is clear from the choice of materials for our test assemblies that we wished this test to show more than just embrittlement. Cadmium, whether electroplated or mechanically plated, is relatively inert to the bi-metallic influence of common steel, stainless steel and aluminum alloys, even in highly corroding atmospheres, and all of the test platings we ran were subject to this bi-metallic assembly test.

One further note on the use of the assemblies as a test fixture: You will recall that the rings are loaded in the radial direction to some 205,000 lbs. P.S.I. Since each assembly was corrosion-tested, it is obviously a very good test for stress-corrosion as well: Did the high working stresses increase the rate of corrosion on the plated parts or, alternately, did any corrosion which occurred increase the stresses to a failure point?

Threaded parts were also plated, assembled in 6064-T4 aluminum threaded blocks with pH 15-7 Mo nuts. These tests were run as part of the bi-metallic tests only.

All assemblies, as well as individual plated pieces, were tested in one of two salt spray cabinets: Ours in our Long Island City laboratories and New York Testing Laboratories' cabinet at Westbury, New York. In effect, we ran duplicate, simultaneous tests, both as a replicate and to eliminate any test bias. Both cabinets and test procedures meet all requirements of ASTM-B-117-64.

Various other parts, threaded and non-threaded, were included in the test for various reasons. Some test parts weighed 600 grams, some test parts were 10" long, many 1-1/2" diameter doughnut-shaped chips were used. We included these parts to make sure our conclusions had general rather than narrow validity.

"Real-life" corrosion testing was done at a testing station located at Jupiter Beach, Florida. The results of tests done at this station vary significantly from the accelerated salt spray tests in several ways, which will be noted as we discuss the results.

The Florida testing station itself was located along the inland waterway approximately 300 yards from the Atlantic Ocean, with a reef overgrown with Australian pines intervening. The location is an interesting one and fencing elements made of hot-dipped galvanized wire frequently have to be replaced in less than two years. Also of general interest, the testing station is located only a short distance from a principal outboard motor manufacturer's testing station.

The Florida tests, which were run in the general period of late June, July, August and early September of this year, included exposure to sun, rain and the very humid salt atmosphere of south Florida in the summer. We were able to establish a very rough correlation to failure of some of the thinner plated parts of roughly one hour in the salt spray cabinet to seven hours in the Florida atmosphere. However, for the heavier plated parts, this correlation is not clear, since failure in many cases on the same basis will take almost a year and we simply do not have enough experience.

It is clear, however, particularly in the case of the assemblies, that the Florida tests give far more meaningful results than the salt spray tests on the relative inertness of a plating to bi-metallic influences and certainly come closer, at least, to relative kind of performance which may be anticipated in real life. On the other hand, the repeatability of specific results in salt spray is unlikely to be matched by any test run in Florida.

The test program, in addition to considering the mechanical properties of the part after plating, the part's corrosion-resistance and the part's inertness in the presence of various metals, considered one of the most significant of all properties of cadmium electroplating, lubricity. Because of the very particular requirements of lubricity and the multiple requirements of various consumers, no standard test was attempted at Waldes; rather we worked through prime producers of threaded fasteners who were able to test the various treatments on the surface of the threaded fasteners to determine whether or not they met specifications for lubricity of cadmium electroplated fasteners. Using GSE test equipment, five large producers determined that the Pollex tin-top plating did, indeed, meet the requirements of a principal automotive manufacturer, both for the amount of torque required to drive the fasteners and for the uniformity of torque requirement from piece to piece and lot to lot. Since we at Waldes are not expert in the tests involved or in the varying requirements of this industry, we will let the test reports speak for themselves.

We are very keenly aware of the desirability of high lubricity on parts such as retainer rings and on parts which are hoppered prior to assembly and in this respect the non-threaded parts performed in an outstanding manner, albeit a subjective evaluation, both in terms of being easier to insert a part in a tight clearance fit and also in terms of speed of hoppering feed compared to other finishes or no finishes at all.

Any discussion of plating quality starts with an assessment of its uniformity of coverage. Our basic device for measurement of thickness is a Dermitron unit. Cadmium-tin mixtures, zinc-tin mixtures and tin-top plating were all measured using the probe designed for measuring cadmium: Pre-test experiment had indicated that this probe most nearly correlated with microscopic thickness measurements of sectioned coated pieces. We believe that this probe is sufficiently accurate for production and quality control of tin-top plating as well as the zinc-tin co-deposit.

The part itself has some tendency to tangle during plating which reduces plating uniformity. It has the reputation in our plant of being a "difficult part" to plate uniformly and smoothly. A typical example of the thickness distribution obtained in measuring a 50-piece sample taken from a lot of Pollex tin-top plating which we intended to be 7 to 8 microns thick (5 to 6 microns of zinc plus 2 microns of tin) can be seen in Fig. 16 below.

TYPICAL DISTRIBUTION OF THICKNESS, POLLEX TIN-TOP PLATING

5μ zinc + 2.5μ tin = $\Sigma\ 7.5\mu$

$6.5\mu = 2$
$7.0\mu = 12$
$7.5\mu = 15$
$8.0\mu = 17$
$8.5\mu = 4$

$\bar{x} = 7.57$

$\sigma = 0.54$

4% of the pieces were in the range 6.5-7.0 microns (undersize) and 8% were in the range 8.0-8.5 microns (oversize). This kind of range is somewhat better than we normally experience in mechanical plating of these parts, but was typical of the test lots and about the same variance as two small cadmium electroplated samples of the same part.

No special treatments prior to plating were given to the rings to prevent embrittlement nor was any attempt made after plating to relieve embrittlement by any known method. The parts were raised to a working stress of 205,000 lb./sq.in. in the radial direction and many parts were held at this load for as long as 12 weeks (in fact, at this writing, most of the parts are still being held under this condition). No failure occurred.

This is no unique incident. In the several years that we have been using our own chemistry and systems for mechanical plating, of the tens of millions of pieces that we have plated, no piece has ever failed in embrittlement testing at Waldes and we know of no customer complaint involving embrittlement on these pieces. We consider this to be a truly remarkable record and we believe that the Pollex plating can be used with no fear of embrittlement and no requirement for post-plating stress relief.

The salt spray corrosion testing in a systematic manner was done in two salt spray cabinets - one in our own laboratory, the second at New York Testing Laboratory - using duplicate sets of samples. Both salt spray tests conformed in every way to ASTM-B-117-64.

In general order of magnitude, for equivalent thicknesses, we find the Pollex tin-top plating to give consistantly superior performance over tin-zinc mixtures in hours to white corrosion; neither has the corrosion resistance of cadmium.

A fair and repeatable evaluation of our salt spray data for the Pollex tin-top plating is summarized in Chart #2, which we believe shows that the Pollex tin-top plating has a usable corrosion resistance for most applications. Many things can be done to improve certain corrosion properties of the Pollex tin-top plating. For example, in the development of a 12 micron thickness, we could improve the resistance to white corrosion by having an 8 micron layer of zinc plus a 4 to 5 micron layer of tin. Systematic evaluation, which is continuing, has not gone far enough to provide us with an equation by which we might estimate the benefits of such a move.

Chart #2

SALT SPRAY CORROSION RESISTANCE

Minimum Coating Thickness*		Type of Plating and Supplementary Treatment	Resistance to Neutral Salt Spray	
			To White	To Red
μm	in.		Corrosion	
50.0	.002	Zinc	196	800
25.0	.001	Plus	160	400
13.0	.0005	Tin	120	168
8.0	.0003	Plus	96	140
5.0	.0002	Chromate	72	96

* The top 2.5μ (.0001") of coating is tin

The bi-metallic assemblies in salt spray show clearly that the Pollex tin-top plating performs identically alone or in the bi-metallic ambience under the severe corroding conditions of salt spray. No battery action or white corrosion appeared prematurely due to the bi-metallic ambience.

The tests in Florida were more interesting and informative in many ways than the tests run in salt spray. Though the general relationships were the same in salt spray and in the Florida tests, we were able to see more clearly what was happening in Florida. For example, the rate at which white corrosion products were formed and the way in which they spread over both the plated part and the surrounding parts was not impeded by masses of salt caked all over the parts and assemblies, and thus we were able to see very clearly that

1) The formation of white corrosion products on the tin-zinc mixtures was about the same as the formation of white corrosion products on zinc alone, and both occurred much earlier than on the Pollex tin-top plating, and

2) In the bi-metallic assemblies, white corrosion products were far more severe for the tin-zinc mixture than they were on the parts plated with the tin-zinc mixture but tested alone rather than in an assembly. The white corrosion products spread over the 430 stainless shafts. From the data it appears that the bi-metallic ambience increased the rate at which white corrosion products formed on the tin-zinc plating mixture and also affected the amount of total white corrosion products formed in any time period. The Pollex tin-top plating again performed well in these circumstances, showing no tendency to form white corrosion products prematurely as a result of the bi-metallic ambience.

We tested a few pieces coated with a popular organic coating in this test and found a most severe battery action which occurred very rapidly, most particularly again with the 430 stainless steel in the presence of aluminum.

It seems to us that this test of performance in a bi-metallic ambience is a most important one in trying to evaluate the performance of an alternative to cadmium electroplating. For example, many of our snap ring parts are used on die cast aluminum and magnesium housings, on stainless steel shafts or housings, and in mixed metallic ambiences in both the automotive and marine motor industries. Many of our customers have traditionally insisted on cadmium plating because of this and our Florida tests have showed how correct they are.

Summing up the corrosion testing, we think that both the salt spray and the Florida testing show that the Pollex tin-top plating has a good corrosion resistance, that it is relatively inert in the presence of a bi-metallic ambience and that for most instances, it appears that it will be a very good real-life replacement for cadmium electroplating.

Lubricity tests were performed by five major manufacturers of locknuts. Basic tests were performed on 8 mm, 10 mm and 14 mm size locknuts in several different deformations. A total of 40 lots were plated with the Pollex tin-top plating for the five manufacturers.

It has been reported to us that all of the samples evaluated by the five manufacturers from the 40 lots fall within the torquing limits of cadmium on the particular product involved and that performance was reliable from lot to lot and from piece to piece within the lots. The test report of one of the manufacturers is appended to this paper.

As a result of the testing done for lubricity, a major automotive manufacturer has indicated acceptance of this finish for the threaded fastener industry as an alternative to cadmium electroplating and we have been invited to propose a tentative standard for the finish. I think that this speaks loudly for the lubricity quality of the process and tells more than anything else I can state.

One very important consideration in evaluating any plating is the cost ratio of this plating in comparison with cadmium electroplating. A careful one-week analysis of an automatic cadmium electroplating line with a basket capacity of 1/2 cu. ft. was made at the Empire Plating Company in Cleveland, Ohio. A further very exhaustive analysis of the costs of the Pollex tin-top plating of almost a comparable thickness was made. All costs were related to a cap screw with a surface area of .8 sq.ft./lb. and a bulk density of 200 lbs./cu.ft. Referring to Chart #17, we assume certain standard costs for the metals involved, for electricity, for water and for labor. We then constructed a weighted cost for the cap screws, using all available data since, unhappily, there were not enough cap screws to run both processes for a week. Both lines were capable of producing in the neighborhood of 1800 lbs. per hour with approximately the same amount of labor. Again, referring to Chart #17, we see that the costs of the two operations are not distinctly different for the basic groups of chemicals, metal, water, labor, maintenance, and there is a small additional charge which accrues to mechanical plating for beads and defoamer; the largest single difference in the costs comes in the electricity. With rising costs per kilowatt hour, electricity has now become a preponderant factor in the cost of electroplating.

The cost bias in favor of the Pollex plating over the cadmium electroplating is very real and very genuine, but it assumes a minimum thickness of 7 to 8 microns and it assumes a relatively large load. This cost analysis is based on 1800 lbs. and for cost parity, at least 1200 or 1300 lb. loads would have been necessary.

Since the cost of the Pollex plating is virtually the same for 5 microns as for 7.5 microns but the cost of cadmium electroplating goes down for a lower thickness, it becomes clear that the cost advantage of Pollex over cadmium electroplating will start only with platings thicker than 6 or 7 microns. However, the additional cost, for example, of 12 microns over 7.5 microns for Pollex is small, being only the additional cost of the zinc powder; thus, the advantage of the Pollex plating over cadmium electroplating will increase as the plating requirement becomes thicker.

The same figures developed for other parts during this study showed approximately the same advantage of the Pollex plating, noting only that as the part grows substantially larger, the advantage of the Pollex plating would probably increase. In general, it is fair to say that as a substitute for cadmium electroplating, the Pollex plating with coatings of 6 microns or thicker will enjoy a cost advantage over cadmium electroplating and this advantage will increase rapidly as the coating requirement increases in thickness.

CHART #17

PLATING - DIRECT COSTS PER LB.
CAP SCREW, .8 SQ.FT./LB., 200 LBS./CUBIC FOOT

	* 7.5μ POLLEX TIN OVER ZINC	6.5μ CADMIUM ELECTROPLATE
CHEMICALS	.0128	.0079
METAL	.0360	.0335
WATER	.0001	.0010
LABOR	.0097	.0097
MAINTENANCE	.0013	.0018
BEADS & DEFOAMER	.0018	
ELECTRICITY	.0010	.0229
Σ	.0627	.0768

* Based on 1800 lb. loads

ASSUME

ELECTRICITY = $.06/KW HOUR

CADMIUM POWDER = $3.54/LB.

ZINC POWDER = $.52/LB.

WATER = $.72/100 CUBIC FEET

LABOR = $10/HOUR

TIN = $5.20/LB.

Again, since it seems probable that because

1) the ability to handle larger and larger loads of mechanical plating will increase in the future, and

2) the cost of energy will probably increase at a somewhat faster rate than most of the other plating costs

it seems probable that in the near and distant future the cost effectiveness of the Pollex plating will grow relative to cadmium electroplating.

One last point concerning costs: Many heat-treated parts require energy-consuming stress relief after electroplating. All of our experience and all of our test results indicate that no one need stress-relieve any Pollex plating after plating in any circumstances of which we can conceive. This is an important cost consideration, both for material-handling and energy consumption. These have not been evaluated in our cost comparison, but it is obvious that this factor increases the cost effectiveness of the Pollex tin-top plating over cadmium electroplating.

In considering cost effectiveness of this plating, two significant factors have been omitted:

1) The cost of the capital equipment involved. Based on current costs, the capital equipment needed to perform at a rate comparable to the automatic cadmium electroplating line we studied at Empire Plating Company, completely installed, is in the range of $125,000 to $130,000. The replacement cost of the electroplating line is estimated at $300,000.

2) Overhead in any fair cost assessment will be in large part a function of the floor space used; while the particular work-handling requirement of any system has to be accounted for to fairly evaluate all the floor space required, the machinery described in item 1 above will occupy approximately 660 sq.ft. of floor space, approximately the same as the automatic cadmium electroplating line.

It seems probable that basic overhead cost assignment per pound would be approximately the same as the existing cadmium electroplating line and that amortization of equipment would be approximately half that required for an automatic cadmium electroplating line.

We draw the following conclusions from our search for a replacement for cadmium electroplating:

1) That we have found a worthy successor for many applications presently done by cadmium electroplating. In our Pollex tin-top plating, this plating should cost slightly less than cadmium electroplating for large bulk orders. It should have equal or greater lubricity. It should have good corrosion-protection against white and red corrosion and is relatively inert against aluminum, stainless steel and various aluminums and stainless steels and combinations thereof. This plating

has the advantage that it can be done in many of the existing mechanical plating set-ups, requiring only know-how and chemistry, so that it can truly become available in various areas within a reasonable time period.

2) Basic zinc and tin thicknesses can be manipulated to increase lubricity, increase resistance to white corrosion, increase dielectric properties, to cover any needs.

3) The Pollex plating can be produced with absolutely no liquid effluent. Equipment and techniques for doing this plating are commercially available at this time and await only sufficient interest on the part of producers. The economics of the pollution-free process are cost effective in every sense of the word.

4) We believe there will be some continuing need for cadmium plating where extreme corrosion protection is required and organic finishes cannot be used because of the lubricity requirement, dielectric requirements, temperature requirements, etc. Such plating can be produced in our pollution-free system and can be produced in any desired thickness, thus for the first time extending the possibility of almost infinite corrosion protection. The Pollex tin-top finish, which can also be extended to great thicknesses, also provides greatly extended protection.

We have a process which can be done in many existing mechanical plating stations, in a uniformly good manner, producing a uniformly high quality product. Happily, the process is not a difficult one and is not sensitive to the kinds of things which cost a great deal of money.

The Pollex anti-pollution system is a patented process of Waldes Kohinoor, Inc. The Pollex tin-top plating is in a "patent applied for" status.

Attach.

APPENDIX I

LUBRICITY TEST WITH AIR STALL GUN

M 14 LOCKNUT - FIRST INSTALLATION

TYPE	RANGE IN INCH LBS.
	Max. Allowable: 274 in. lbs.
A	234-528
A + wax	168-336
B	232-488
B + wax	156-288
C	192-396
C + wax	156-318
Pollex tin-top, 8µ	102-180
Pollex tin-top with wax, 8µ	90-165
D	240-540
D + oil	244-576
D + wax	144-420

Twenty pieces of each finish were tested.

Note: Johnson's 111 Wax used in all instances where wax is used.

A Practical Wet Impact Alternative to Cadmium Electroplating.

DISCUSSION PERIOD

MR. GROBIN: Allen Grobin, IBM Corporation.

I notice that you have a sacrificial metal, zinc, between two other metals. Now, is there any bake process in there that would account for any alloying of tin and zinc layers, so you don't get creeping corrosion separation of the layers.

MR. COCH: Yes. I can bring that out just a little bit for you. The zinc in this particular case was taken from powdered zinc, which is approximately three microns in diameter. The mechanical plating process, as you know, basically impacts against the grain of the zinc and elongates it and it is in effect stuck with glue onto the part.

The tin is taken from atomic tin, not by simple reaction. The whole chemical ambience is such that you get the kind of alloying that you are talking about.

I cannot possibly comment on the thickness, but there is the kind of alloying you are talking about. The coating was completely unsuccessful with the powdered tin.

MR. GROBIN: I would agree with your observation. Once there is alloying, you are going to get creeping corrosion separation. We have observed this ourselves. You do recognize you have alloying there.

MR. COCH: Yes. Incidentally, we tried to guard against this. We have done a number of other tests. A part of contraction expands very severely under tremendous load. Both adhesion and cohesion of all plating layers is always a problem to us.

For example, the ten-inch part that you saw which goes into aerospace has a diametric contraction in the neighborhood of over an inch, and, of course, you have tremendous loading. The inside diameter loads very severely in compression, the outside tension. We did a tremendous amount of these flexion tests looking for just this kind of a problem, and we didn't find any.

The tests are ongoing in Florida. We put out the first pieces on the first of July, but we will continuously update the reports on what we find there.

MR. HEIDERSBACH: Bob Heidersbach, Ocean Technology Incorporated.

I have two questions. One, as I understand it, you are talking about a ferrous or aluminum substrate with zinc topped by tin.

MR. COCH: No, sir. I am talking about only a ferrous substrate with zinc topped by tin. We have not done this with aluminum.

MR. HEIDERSBACH: Why don't you compare that to a simple tin coating as well?

MR. COCH: In what way?

MR. HEIDERSBACH: Well, as I understand it, you have a tin surface.

MR. COCH: A tintop surface, yes, sir.

MR. HEIDERSBACH: Is this essentially a noble metal coating, which you are comparing with sacrificial coatings, such as any of the other metals that have been discussed so far today?

MR. COCH: Yes.

MR. HEIDERSBACH: Okay, and you have two different situations there. Have you tried deliberately induced stress environmental tests of any sort?

MR. COCH: We have not. We have talked about the possibility of eroding our parts intentionally. That would be to take one of the large parts, and draw it in with a pair of pliers until the points were touching. Then put a deliberate scratch through it to see what the results are.

One of our customers uses such a part. It's about an inch and a half at the end of a long tube. It's on an inboard-outboard motor and it's subject to repeated impacts at an ambience of 200 degrees Fahrenheit. It is sometimes sprayed. You are all familiar with the beautiful blue they spray it with that doesn't coat the snaplink completely. This is almost the situation you are talking about, in many ways, because it lets all the action go to one place. Now, I have induced these people to try three or four of these parts, which I think will come very close to what you are talking about. All of our parts get a certain amount of scratching when they are installed because they have to be done with pliers or some other way. We are very conscious of this problem.

Alternative Materials and Processes

Session II

Tuesday Afternoon 4:20

ELECTRODEPOSITION OF ZINC-NICKEL ALLOY COATINGS

J. W. Dini
H. R. Johnson
Sandia Laboratories
Metallurgy & Electroplating Division
Livermore, California 94550

One possible substitute for cadmium in some applications is a Zn-Ni alloy electrodeposit. In the past, thermally prepared coatings of Zn-Ni coatings have been used under the trade name Corronizing. They were prepared by the interdiffusion of separately deposited Ni and Zn coatings. The fact that the diffusion coating has had applications indicates that an electrodeposited Zn-Ni coating would also have applications if a convenient method of deposition could be developed. One of these applications could be as a substitute for cadmium.

Earlier work has already shown that electrodeposited alloys containing about 85% zinc and about 15% nickel provide noticeably better corrosion resistance than pure zinc. Present work supports this finding and also provides a comparison with electroplated cadmium in salt spray. Data on operation of the solution is presented including influence of current density and temperature on deposit composition and corrosion resistance. A method of chromating the deposits was developed and this also improves corrosion resistance.

Based on the work reported in this paper, future efforts with electrodeposited Zn-Ni coatings are warranted since this deposit looks like a viable substitute for cadmium.

ELECTRODEPOSITION OF ZINC-NICKEL ALLOY COATINGS*

J. W. Dini
H. R. Johnson
Metallurgy and Electroplating Division 8312
Sandia Laboratories
Livermore, California 94550

ABSTRACT

One possible substitute for cadmium in some applications is a zinc-nickel alloy deposit. Previous work by others showed that electrodeposited zinc-nickel coatings containing about 85% zinc and 15% nickel provided noticeably better corrosion resistance than pure zinc. Present work supports this finding and also shows that the corrosion resistance of the alloy deposit compares favorably with cadmium.

---

*This work was supported by the United States Energy Research and Development Administration. Contract Number AT-(29-1)-789.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of the following: J. R. Helms, 8312, plating, T. L. Bryant, 8312, metallography, G. M. Giovacchini, 8313, X-ray diffraction, and P. Dean, 8265, technical writing

ELECTRODEPOSITION OF ZINC-NICKEL ALLOY COATINGS

Introduction

Thermally prepared coatings of Zn-Ni have been obtained by the interdiffusion of separately deposited nickel and zinc coatings and used as a protective coating for steel under the trade name Corronizing.[1] The commercial use of the diffusion coating indicates that electrodeposited Zn-Ni coatings also should have applications, if a convenient method of deposition could be developed. One of these applications could be a substitute for cadmium.

The literature on the topic of Zn-Ni plating up to 1960 was covered by Brenner[2] in his treatise on alloy deposition. Since 1960, very little has appeared on this subject. Hammond and Bowman[3,4] were granted patents in 1961 and 1962. Kudryautsev[5] reported on deposition from cyanide and ammoniacal solutions in 1964. Domnikov[6] reviewed some Russian work in 1965, Roehl[7] was granted a patent in 1969, and Roehl and Dillon[8] a patent in 1971. These latter two patents were the starting point for the work described in this paper. Roehl[7] reported that in salt spray tests, 92% Zn-8% Ni alloy coating was three to four times as corrosion resistant as electrodeposited zinc or hot-dipped zinc (Figure 1). Based on the results reported in the literature and the fact that zinc-nickel coatings have shown promise at Sandia Laboratories, Livermore, in protecting uranium alloys from corrosion, it was deemed worthwhile to investigate zinc-nickel alloy plating in further depth. The present study was divided into two parts. The first portion consisted of determining the optimum operating conditions for the electroplating process. The factors evaluated were the influence of current density and temperature on deposit appearance, composition, stress, and efficiency. The second portion of the study evaluated the proposed zinc-nickel coating in a salt fog environment. To provide comparison data, unalloyed zinc and cadmium coatings were also evaluated in the same environment. A salt fog environment was selected for this study because previous investigations had demonstrated the superiority of cadmium over unalloyed zinc in this test.

Selection of Operating Conditions

General

The work reported herein was done with 10-litre solutions of the composition listed in Table I. The solution is basically Roehl's[7] with some changes. He used the chloride salts of zinc and nickel whereas we used zinc sulfate and nickel sulfamate. The reason for this change is that one potential application for Zn-Ni coatings is corrosion protection for uranium and its alloys, and these materials are notoriously attacked by chlorides.

A few cursory experiments revealed that nickel sulfate could be substituted for the nickel sulfamate. If this coating system were to be used in production, the sulfate would be less expensive than sulfamate. Roehl[7] recommended a small amount of acetic acid as a buffer to promote ease of pH control. We found this to be unnecessary, and furthermore discovered as a result of some Hull cell tests that acetic acid reduced the covering power of the solution. Zinc anodes were used for most of the work, but alloy anodes of the approximate composition Zn-10 Ni would probably be quite suitable.

A wetting agent (sodium lauryl sulfate) was used to lower the surface tension of the solution to eliminate pitting. The importance of this ingredient is shown in Figures 2a and 2b, which compare deposits produced in solutions with and without wetting agent. Heavy pitting was evident in the deposit obtained from the solution containing no wetting agent, whereas no pitting was evident when the wetting agent was present. An additional benefit of the wetting agent is that it improves the appearance of the deposit and has a grain refining effect.

Steel panels 6.4 x 10.2 cm (2.5 x 4 in.) were used as the plating substrates. Steel was selected because the red rust produced on unprotected surfaces in salt spray gives a good indication of the corrosion process occurring.

The parameters used to evaluate the operating conditions were: influence of current density and temperature on deposit appearance, composition, stress and efficiency.

Influence of Current Density and Temperature

As illustrated in Figure 3, deposits with the highest nickel contents were obtained at the lowest current densities. Likewise, the higher the plating temperature, the higher the nickel content of the deposit. The appearance of the deposits produced at 27 and 50°C did not change much over the current density range of 54 to 538 A/m^2. However, a noticeable difference was obtained at 93°C. Figure 4 shows that deposits plated at 93°C were black at 54 A/m^2, grey at 538 A/m^2 and grey-black at 269 A/m^2. The black coloration is attributed to the higher amounts of nickel plated out at the lower current densities.

Repeated measurements revealed that efficiency* at 54 A/m^2 was greater than 100%, which is indicative of either material being occluded in the deposit or autocatalytic deposition; we choose to believe the former. There are indications that deposition at the lower current densities was accompanied by heavy oxides and hydroxides. Gas and carbon analysis of some deposits revealed noticeably higher impurity content at lower current densities. This is especially evident when comparing deposits produced at 54 and 538 A/m^2 (Table II). There was no weight change in the deposits after heating at 150°C for 24 hours, which ruled out trapped moisture. For the 54-A/m^2 samples, deposition above 60°C was accompanied by heavy gas evolution and efficiency increased with temperature (Figure 5). This phenomenon was not as obvious at 269 A/m^2 because at this current density efficiencies greater than 100% were not obtained until plating temperatures greater than 70°C were used. At 538 A/m^2, efficiency was 100% over the temperature range of 27 to 93°C (Figure 5).

---

*The efficiency measurements were based on the standard established by a copper coulometer connected in series with the Zn-Ni plating solution. The coulometer contained 200 g/l of copper sulfate, 100 ml/l (specific gravity 1.83) of sulfuric acid and 50 ml/l of absolute ethyl alcohol. To calculate the efficiency, the deposit composition was first determined by atomic absorption analysis, and then electrochemical equivalents of the alloy were calculated by the reciprocal method described by Lowenheim.[9]

X-Ray Diffraction

The Debye-Scherrer method was used to obtain X-ray information on some Zn-Ni deposits. The results of this analysis, along with the results from the computer program SEARCH[10] revealed a major line of zinc sulfate hydroxide hydrate, $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$, some minor probable Zn lines, and some unidentified lines. In addition, the SEARCH program also indicated that NiO and $NaNiO_2$ could be present in the sample.

Stress

Stress in the deposit was measured with the rigid-strip technique described by Borchert.[11] Temperature was varied from 49 to 88°C and current density from 27 to 269 A/m^2. The data, included in Table III, show that the stress was quite low, less than 35 MN/m^2 (5000 psi) and influenced very little by variations in current density or temperature.

Salt Fog Tests

Samples and Plating Solutions

For the salt fog tests, steel panels were plated with 2.5, 7.5, 12.5, and 25 μm (0.1, 0.3, 0.5, and 1.0 mil) of cadmium, zinc, and zinc-nickel alloy. The cadmium was plated in a cyanide solution and the zinc in an acid chloride solution according to formulations and operating conditions listed in Table IV. Some of the panels from each set were chromated prior to salt fog testing. Some comment should be made on the chromating of zinc-nickel deposits. A number of proprietary immersion processes were tried with no success, inasmuch as either no apparent chromate film was formed or if one was formed it was non-uniform and/or non-adherent. Use of electrical current in Macro Drab No. 6* which is a proprietary process for zinc and cadmium, did provide a uniform adherent film similar in appearance to the films typically seen on zinc. Parts were cathodically treated in this solution at 9 volts for 1 minute at 32°C.

All samples were placed in plastic holders that inclined them 15 degrees from the vertical. They were exposed up to 500 hours in a cabinet with a 5 percent salt fog environment at 35°C (95°F), per ASTM B117-49T.

---

*Mac Dermid, Inc., Waterbury, Conn.

Results

Unchromated Panels

The salt spray results are summarized in Tables V and VI and presented pictorially in Figures 6-11. The panels with no chromate clearly showed the inferiority of unalloyed zinc when compared with cadmium or zinc-nickel alloy coatings in salt spray. Heavy white corrosion products commonly referred to as "white rust"* were obtained very quickly on the pure zinc-coated panels, and rusting started much quicker than on the cadmium or zinc-nickel coated panels. Corrosion was so heavy on the pure zinc panels that none of these were left in salt spray for more than 192 hours, whereas all but the thinnest cadmium and zinc-nickel coatings were exposed for 500 hours. The zinc-nickel coatings exhibited a moderate amount of white corrosion products, considerably less than the pure zinc coatings but more than the cadmium coatings. Figure 6 compares the white rust on unchromated panels after 24 hours. The red rusting on the zinc-nickel deposits was about equivalent to that observed on the cadmium panels. The zinc-nickel coating deposited at 54 A/m^2 was slightly more corrosion resistant to red rusting than the panel plated at 269 A/m^2.

Chromated Panels

The chromated zinc-nickel panels plated at 32°C were not as corrosion resistant during 500 hours of salt spray as those plated at 60°C. This is probably because less nickel is included in the alloy when deposition takes place at lower temperatures (see Figure 3). For the samples plated at 60°C, some rust was evident on the panel with 2.5 μm of coating plated at 54 A/m^2; no rust was evident on the companion panels plated at 269 A/m^2.

---

*These corrosion products are mixtures of zinc hydroxide and zinc carbonate.

The zinc-nickel panels plated at 60°C were more corrosion resistant than the acid zinc deposit. Zinc-nickel coatings plated at a current density of 269 A/m^2 exhibited no rusting for the duration of the test, whereas acid zinc coatings and the zinc-nickel coatings plated at 54 A/m^2 did show some rusting. A coating of 2.5 μm of acid zinc started to rust at 360 hours, and at 500 hours the 7.5-μm thick coating of this deposit also started showing red rust. The zinc-nickel deposit plated at 54 A/m^2 showed red rust on the 2.5-μm thick coating at 360 hours but no red rust on the remainder of the panels after 500 hours.

Comparison of zinc-nickel samples with cadmium plated samples showed that the zinc-nickel deposits plated at 60°C performed better than the cadmium panels, especially for a deposit thickness of 2.5 μm. Zinc-nickel deposits plated at 32°C, however, were slightly inferior to the cadmium plated panels. After 500 hours of exposure, heavy red rust was evident on the 2.5-μm thick cadmium panel; no rust appeared on the zinc-nickel coating plated at 269 A/m^2, and only a small amount of rust was evident on the zinc-nickel panel plated at 54 A/m^2.

Summary

Zinc-nickel alloy coatings appear to be a potentially viable substitute for cadmium coatings. Salt fog exposure tests showed that zinc-nickel coatings performed at least as well as cadmium in protecting steel from corrosion. Data on operation of the solution is presented, including the influence of current density and temperature on deposit composition and stress.

Although this effort has demonstrated that Zn-Ni coatings are a potentially viable system for protecting steel from corroding, much work remains to be done to economize the process. Further work is needed on the composition and operating conditions of the solution. Nickel sulfate can be substituted for the nickel sulfamate used in this work but compositional ranges of both the nickel and zinc salts are presently unknown. The solution can probably be operated with much less nickel and still produce satisfactory deposits, but this would have to be proved. Additional effort should also be expended to define the most economical current density and temperature. Also, it is very important to evaluate the potentiality of barrel plating Zn-Ni, since much of the cadmium is plated in this fashion. Further work would also be needed to determine the anode system (pure zinc with occasional additions of nickel, or zinc-nickel alloy anodes) most economical for this solution. Lastly, and perhaps most important, a brightener system would have to be developed if this deposit is ever to really compete with cadmium. Most of the applications for cadmium call for a bright deposit and to try to replace these with a dull zinc-nickel deposit could be an insurmountable task. A bright zinc-nickel deposit would be much easier for users of plated products to accept as a substitute for cadmium.

REFERENCES

1. G. Black, Metal Finishing, 44, 207 (May 1946).
2. A. Brenner, Electrodeposition of Alloys, Volume II, Academic Press, 1963.
3. M. B. Hammond and G. B. Bowman, U. S. Patent 2,989,446, June 1961.
4. M. B. Hammond and G. B. Bowman, U. S. Patent 3,064,337, November 1962.
5. V. A. Averkin, Editor, Electrodeposition of Alloys, Israel Program for Scientific Translation, Jerusalem, 1964, pp. 102-115. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D.C.
6. L. Domnikov, Metal Finishing, 63, 63 (March 1965).
7. E. J. Roehl, U. S. Patent 3,420,754, January 1969.
8. E. J. Roehl and R. H. Dillon, U. S. Patent 3,558,442, January 1971.
9. F. A. Lowenheim, Electroplating and Metal Finishing, 15, 358 (1962).

10. M. C. Nichols, A FORTRAN II Program for the Identification of X-Ray Powder Diffraction Patterns, Univ. of California, Lawrence Radiation Laboratory, UCRL-70078, October 17, 1966.

11. L. C. Borchert, 50th Annual Proceedings American Electroplaters' Society, p. 44, (1963).

TABLE I

ZINC-NICKEL SOLUTION FORMULATION

Zinc Sulfate ($ZnSO_4 \cdot 7H_2O$)	266 g/l
Zinc	60 g/l
Nickel Sulfamate*	190 ml/l
Nickel	34 g/l
Sodium Lauryl Sulfate	0.375 g/l
Surface Tension	35-40 dynes/cm
pH	5.0

*SNR 24 sulfamate nickel concentrate, Allied-Kelite Products Div., the Richardson Co., Des Plaines, Ill.

TABLE II

GAS AND CARBON CONTENT OF ZINC-NICKEL DEPOSITS

Current Density		Carbon①	Hydrogen②	Oxygen②	Nitrogen②
A/m^2	A/ft^2	(ppm)	(ppm)	(ppm)	(ppm)
54	5	2500	170	1200	800
269	25	2200	115	170	105
538	50	1000	44	181	190

①Determined by combustion in oxygen, and then use of a residual gas analyzer.

②Determined by gas fusion.

TABLE III

INFLUENCE OF TEMPERATURE AND CURRENT DENSITY ON STRESS

Current Density		Temperature		Stress①	
A/m^2	A/ft^2	C°	F°	MN/m^2	psi
27	2.5	88	190	24.1	3500
270	2.5	49	120	35.2	5100
270	2.5	88	190	33.4	4850

① Measured by the rigid strip method, Reference 11.

TABLE IV

FORMULATION AND OPERATING CONDITIONS FOR CADMIUM AND ZINC PLATING AND CHROMATING SOLUTIONS

Cadmium		Zinc	
Plating Solution	g/l	Plating Solution	g/l
Cadmium	22.5	Zinc (as zinc chloride)	46
Sodium Cyanide	124	Ammonium Chloride	190
Caustic Soda	19.5	Maz Brightener 8480**	As Recommended by Supplier
Udylyte Bry-Cad #53 Brightener*	As Recommended by Supplier	Maz Brightener 8482**	"
Current Density	161 A/m^2 (15 ASF)	Current Density	259 A/m^2 (25 ASF)
Temperature	27°C	Temperature	27°C
Chromating Solution		Chromating Solution	
Sodium Dichromate	200 g/l	Macro Drab No. 6**	
Sulfuric Acid	6 ml/l		
pH	1.0		
Temperature	25°C	Temperature	27°C
Time	15 s	Time	30 s

*The Udylyte Corp., Detroit Mich.

**Mac Dermid, Inc., Westbury, Conn.

TABLE V

SALT SPRAY CORROSION RESULTS FOR CADMIUM (CYANIDE) AND ZINC (ACID) DEPOSITS[A]

Cadmium							Zinc				
Thickness		Chromate Treatment	Hours in Test				Chromate Treatment	Hours in Test			
Mils	Microns		48	192	360	500		24	72	168	192
0.1	2.5	None	Red Rust [C]				None	Red Rust [D]			
0.3	7.5	None	No Corrosion	Red Rust	Red Rust	Red Rust	None	Heavy White Rust	Red Rust [E]		
0.5	12.5	None	No Corrosion	No Corrosion	Red Rust	Red Rust	None	Heavy White Rust	Heavy White Rust	Red Rust [F]	
1.0	25.0	None	No Corrosion	No Corrosion	White Edge Corrosion	White Edge Corrosion	None	Heavy White Rust	Heavy White Rust	Heavy White Rust	Red Rust [G]
			48	192	336	500		240	360		500
0.1	2.5	Yes [B]	No Corrosion	Red Rust	Red Rust	Red Rust	Yes [B]	Slight White Corrosion	Red Rust		Red Rust
0.3	7.5	Yes [B]	No Corrosion	No Corrosion	White Edge Corrosion	White Edge Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		Slight Red Rust
0.5	12.5	Yes [B]	No Corrosion	No Corrosion	No Corrosion	White Edge Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		White Corrosion
1.0	25.0	Yes [B]	No Corrosion	No Corrosion	No Corrosion	No Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		White Corrosion

[A] See Table IV for solution composition and operating conditions.

[B] See Table IV for chromating details.

[C] Tested for only 72 hours.

[D] Tested for only 24 hours.

[E] Tested for only 144 hours.

[F] Tested for only 168 hours.

[G] Tested for only 192 hours.

TABLE VI

SALT SPRAY CORROSION RESULTS FOR ZINC-NICKEL DEPOSITS[A]

Plating Current Density		54 A/m²				
Plating Temp.		60°C				
Thickness		Chromate Treatment	Hours in Test			
Mils	Microns		24	48	360	500
0.1	2.5	None	Light White Rust	Red Rust [C]		
0.3	7.5	None	Light White Rust	Light White Rust	Red Rust	Red Rust
0.5	12.5	None	Light White Rust	Light White Rust	Light White Rust	Red Rust
1.0	25.0	None	Light White Rust	Light White Rust	Light White Rust	Light White Rust
			24	360	500	
0.1	2.5	Yes [B]	No Corrosion	Red Rust	Red Rust	
0.3	7.5	Yes [B]	No Corrosion	White Staining	White Staining	
0.5	12.5	Yes [B]	No Corrosion	White Staining	White Staining	
1.0	25.0	Yes [B]	No Corrosion	White Staining	White Staining	

Plating Current Density		269 A/m²					
Plating Temp.		60°C					
Thickness		Chromate Treatment	Hours in Test				
Mils	Microns		24	48	240	336	500
0.1	2.5	None	Light White Rust	Red Rust	Red Rust	Red Rust	Red Rust
0.3	7.5	None	Light White Rust	White Rust	Red Rust	Red Rust	Red Rust
0.5	12.5	None	Light White Rust	White Rust	White Rust	Red Rust	Red Rust
1.0	25.0	None	Light White Rust	White Rust	White Rust	White Rust	Red Rust
			24	48	240	500	
0.1	2.5	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	
0.3	7.5	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	
0.5	12.5	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	
1.0	25.0	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	

Plating Current Density		269 A/m²				
Plating Temp.		32°C				
Thickness		Chromate Treatment	Hours in Test			
Mils	Microns		24	144	384	500
0.1	2.5	Yes [B]	Light White Rust	Red Rust	Red Rust	Red Rust
0.3	7.5	Yes [B]	Light White Rust	White Corrosion	Red Rust	Red Rust
0.5	12.5	Yes [B]	Light White Rust	White Corrosion	White Corrosion	White Corrosion
1.0	25.0	Yes [B]	Light White Rust	White Corrosion	White Corrosion	White Corrosion

[A] See Table IV for solution composition.

[B] Cathodic at 9 volts for 1 minute at 32°C in Macro-Drab No. 6, Mac Dermid Inc., Waterbury, Conn.

[C] Tested for only 72 hours.

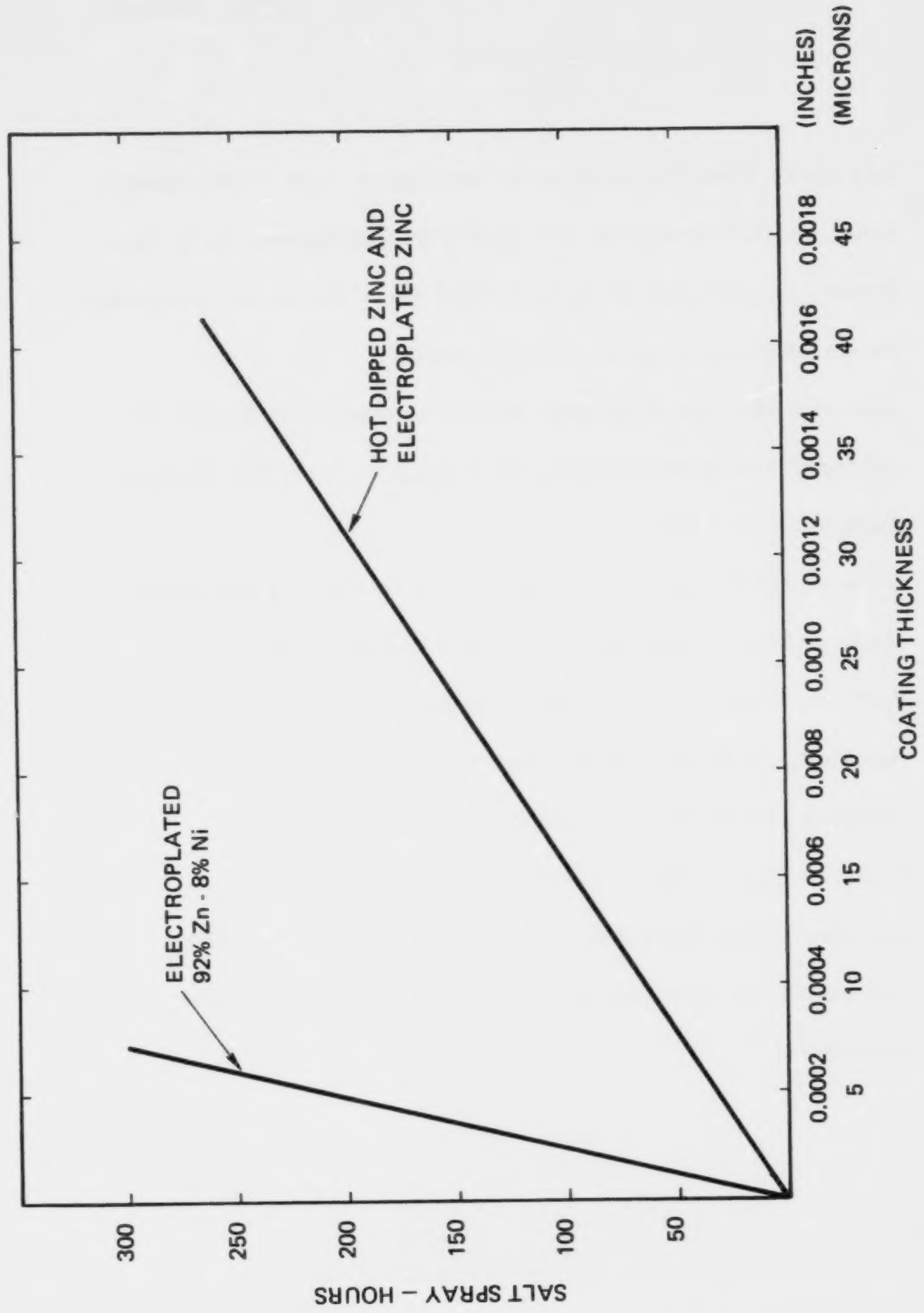
Preceding page blank

FIGURE CAPTIONS

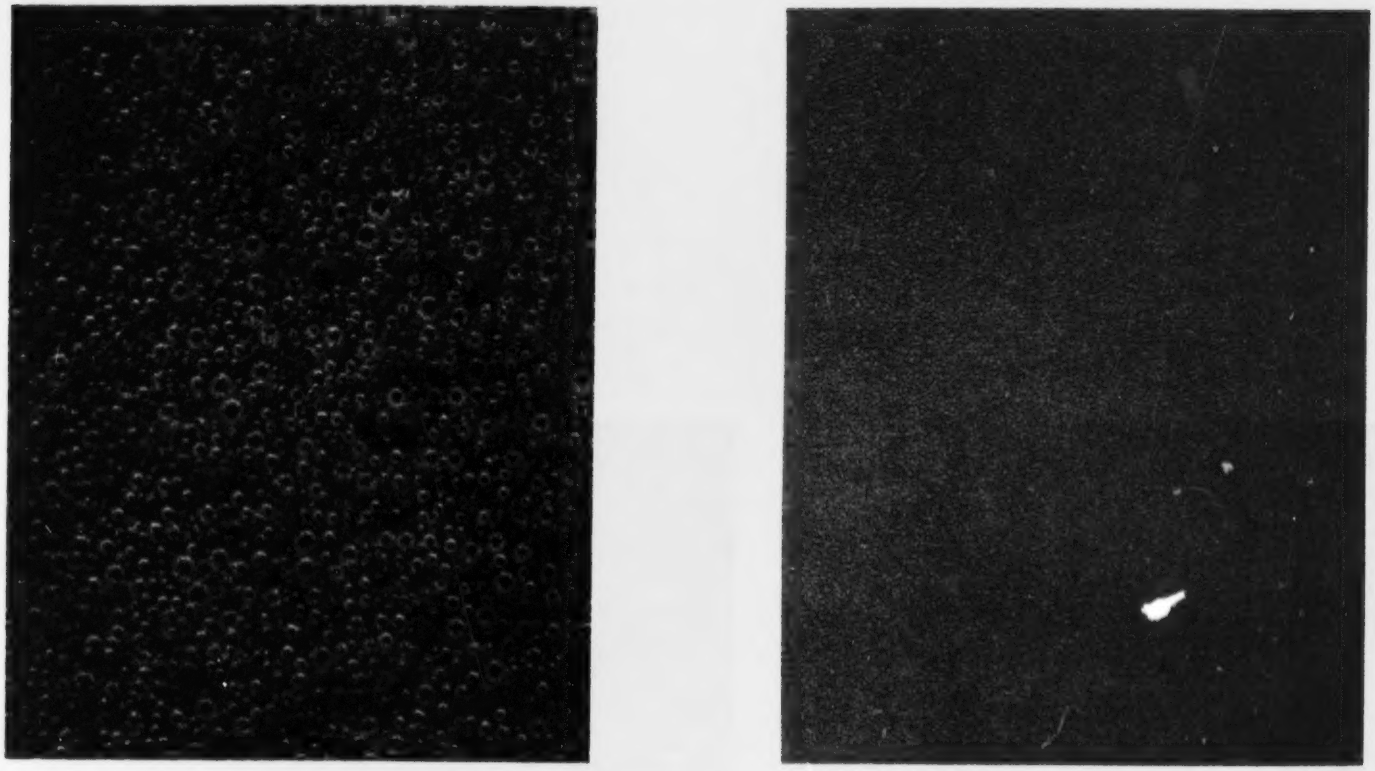
Figure 1.	Salt Spray Test Comparison of Hot Dipped Zinc, Electroplated Zinc, and Electroplated 92% Zn-8% Ni Coatings on Strip Steel
Figure 2a.	Surface Appearance of 100 μ (4 Mil) Thick Zn-Ni Alloy Deposits
Figure 2b.	Cross Sections of Zn-Ni Alloy Deposits
Figure 3.	Influence of Current Density and Temperature on Composition
Figure 4.	Influence of Current Density on Deposit Appearance (Plating Temperature = 93°C)
Figure 5.	Influence of Temperature and Current Density on Efficiency
Figure 6.	Unchromated Panels After 24 Hours in Salt Spray
Figure 7.	Samples Plated in Acid Zinc Solution
Figure 8.	Samples Plated in Cyanide Cadmium Solution
Figure 9.	Samples Plated With Zinc-Nickel (54 A/m^2, 60°C)
Figure 10.	Samples Plated With Zinc-Nickel (269 A/m^2, 60°C)
Figure 11.	Samples Plated With Zinc-Nickel (269 A/m^2, 32°C) After 500 Hours Salt Fog Exposure (all were given a chromate treatment)

Preceding page blank

Dini, Johnson - Figure 1



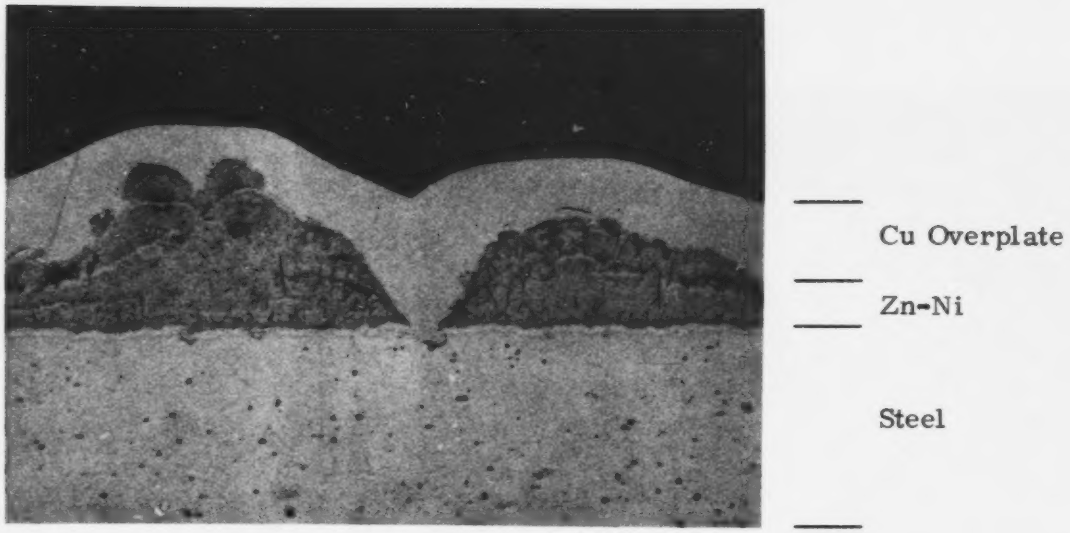
Dini, Johnson - Figure 2a



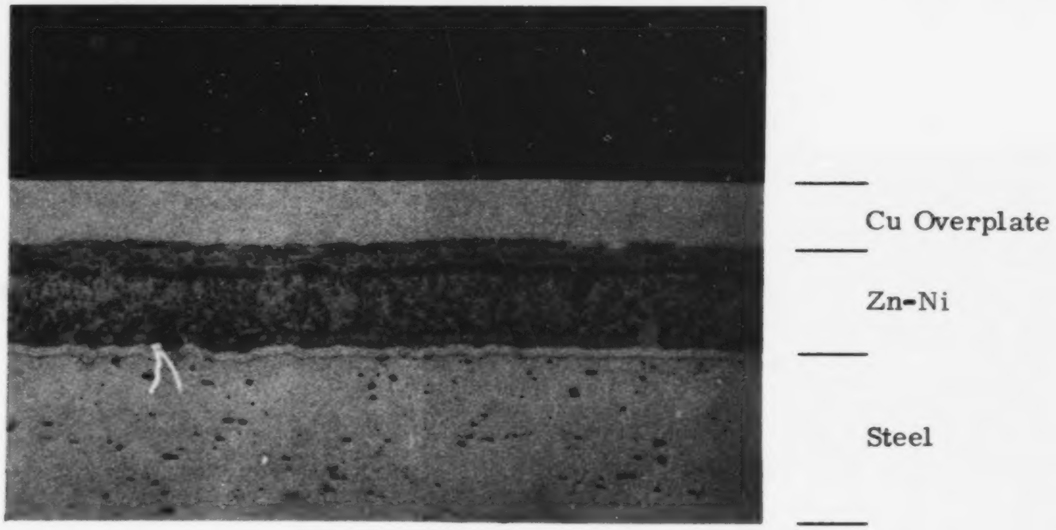
(a) Plated in Solution Containing No Wetting Agent

(b) Plated in Solution Containing Wetting Agent

Dini, Johnson - Figure 2b

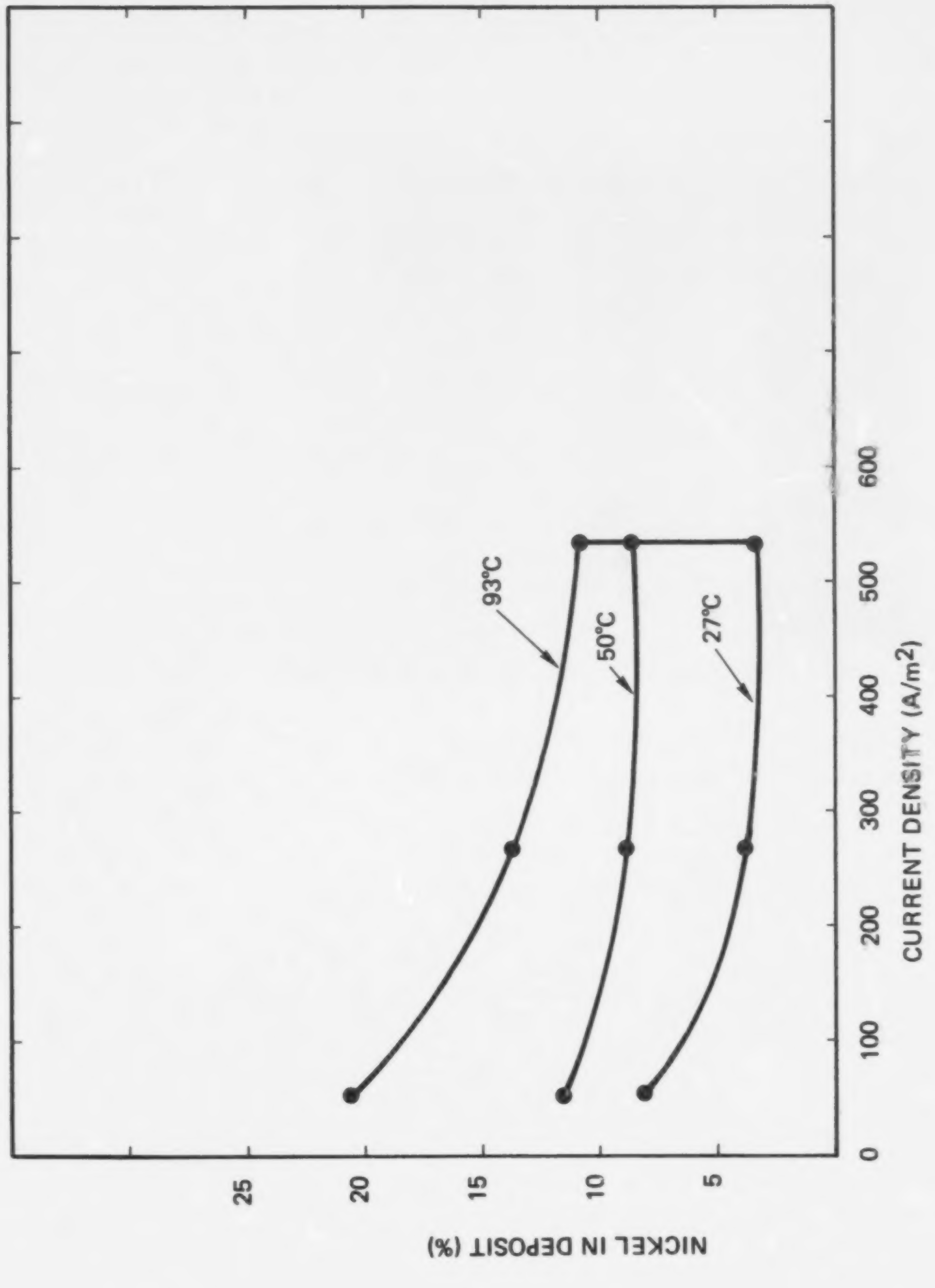


(a) Plated in Solution Containing No Wetting Agent

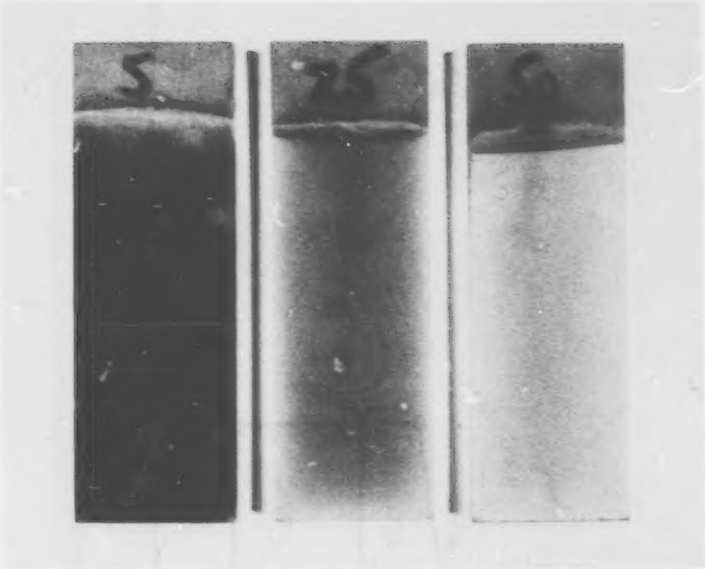


(b) Plated in Solution Containing Wetting Agent

Dini, Johnson - Figure 3

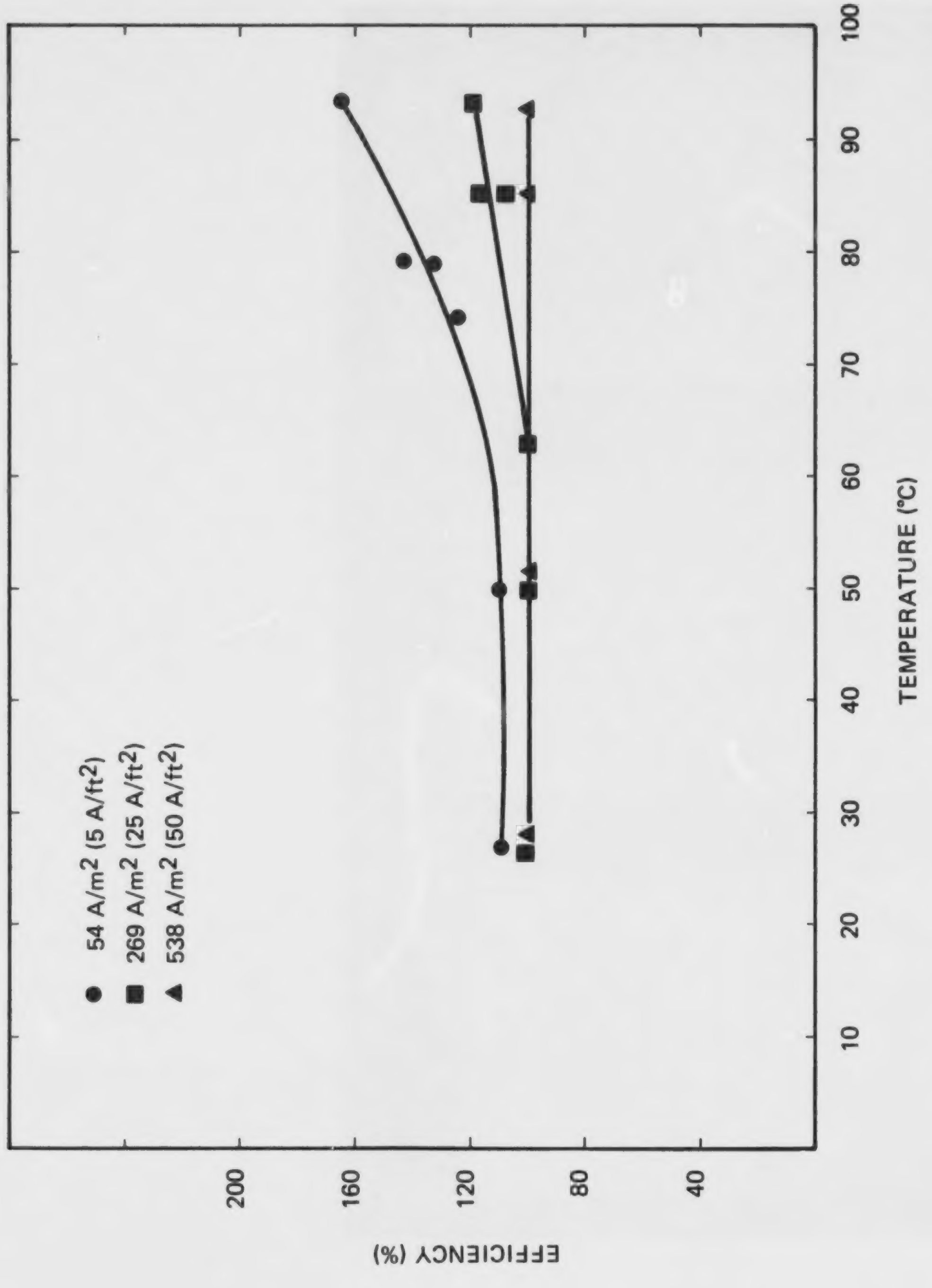


Dini, Johnson - Figure 4

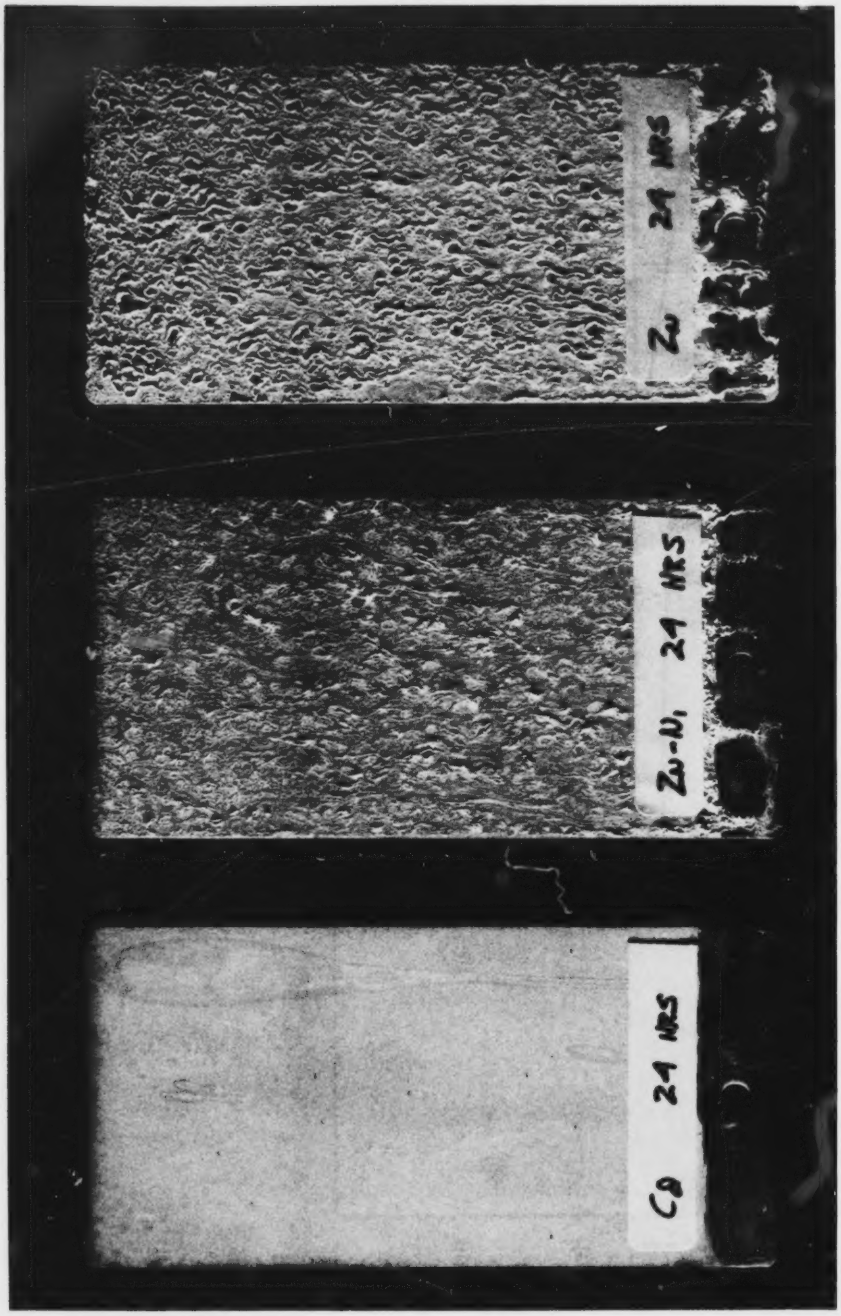


5 asf $54\ A/m^2$ 25 asf $269\ A/m^2$ 50 asf $538\ A/m^2$

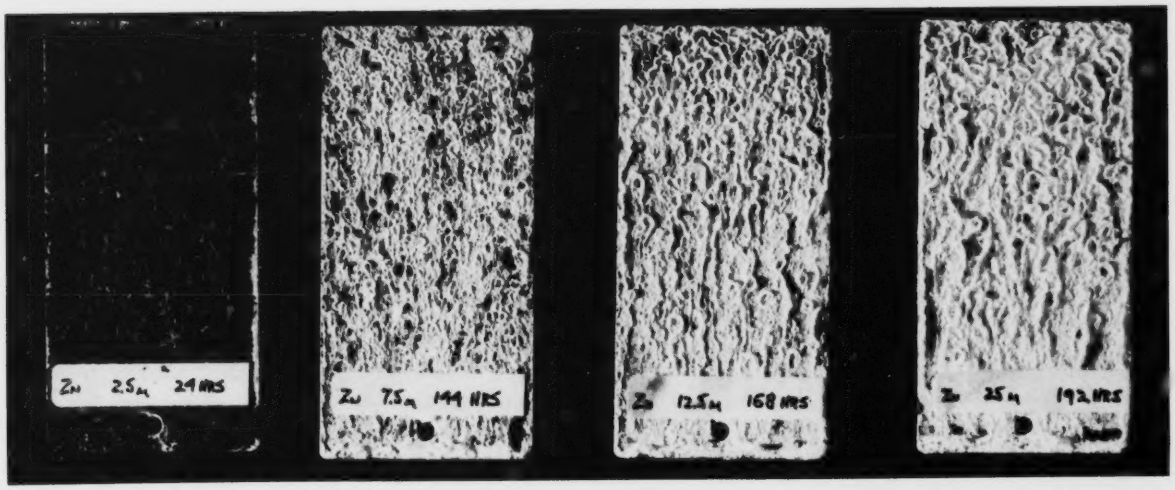
Dini, Johnson - Figure 5



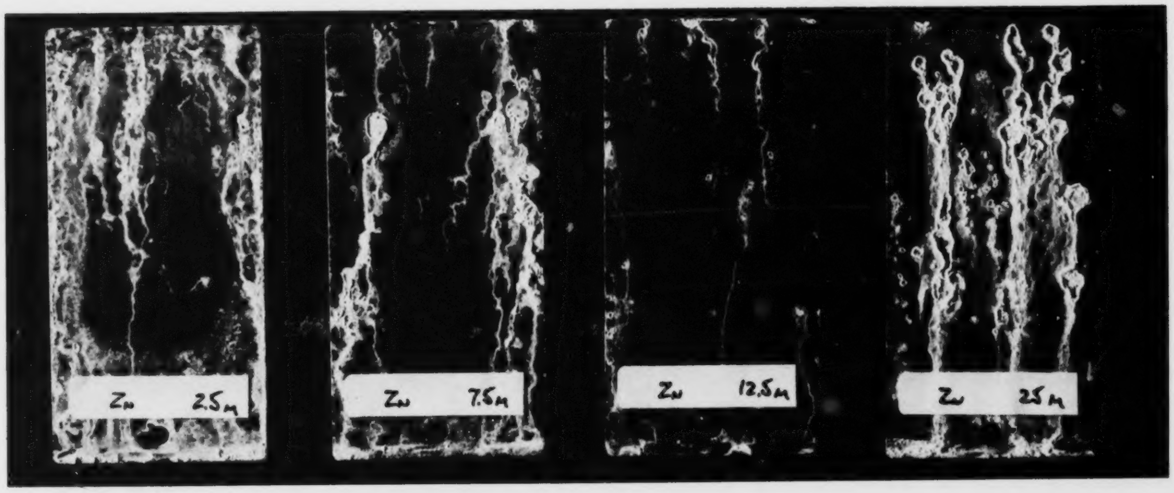
Dini, Johnson - Figure 6



Dini, Johnson - Figure 7

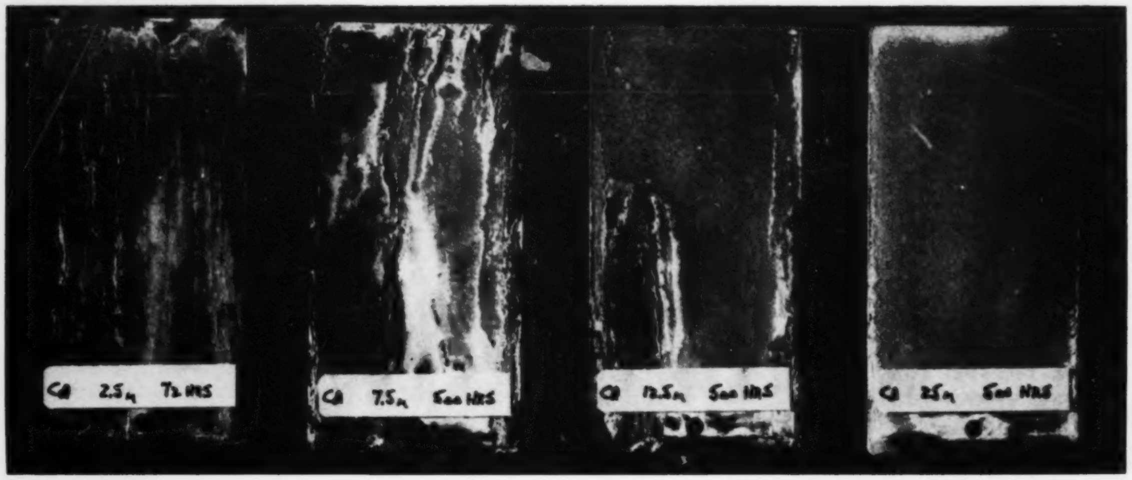


No Chromate Treatment (salt fog exposure time as indicated on panels)

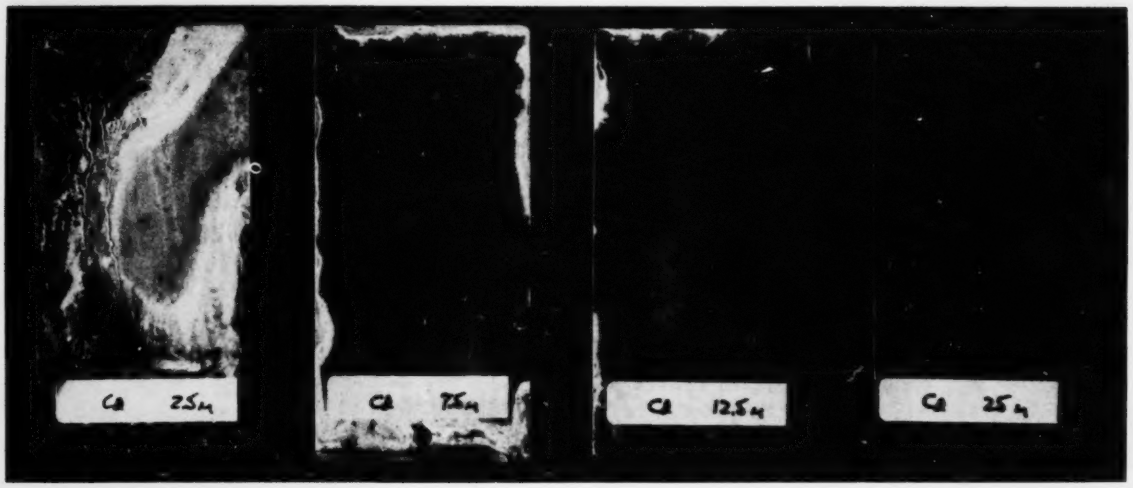


Chromate Treatment (500 hours salt fog exposure)

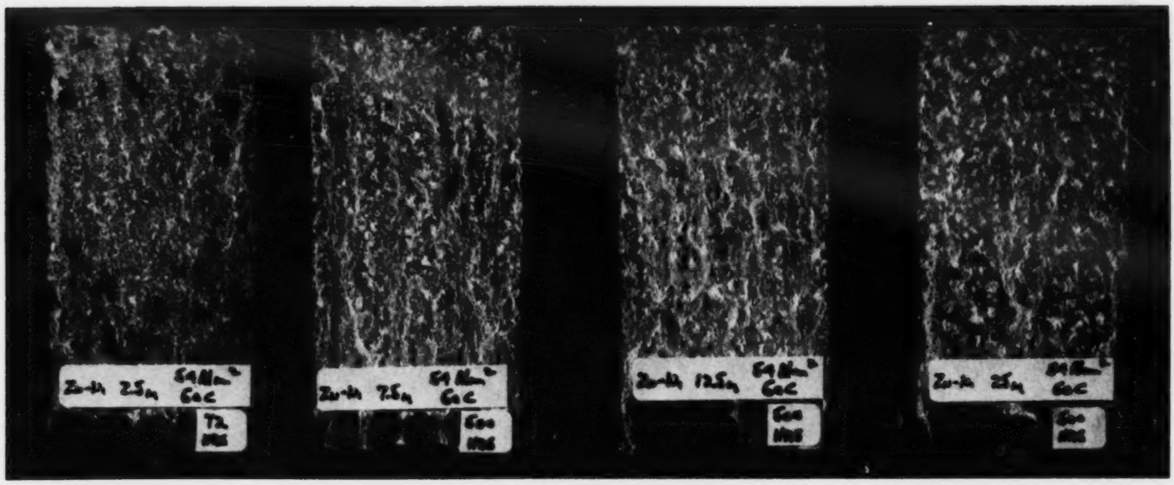
Dini, Johnson - Figure 8



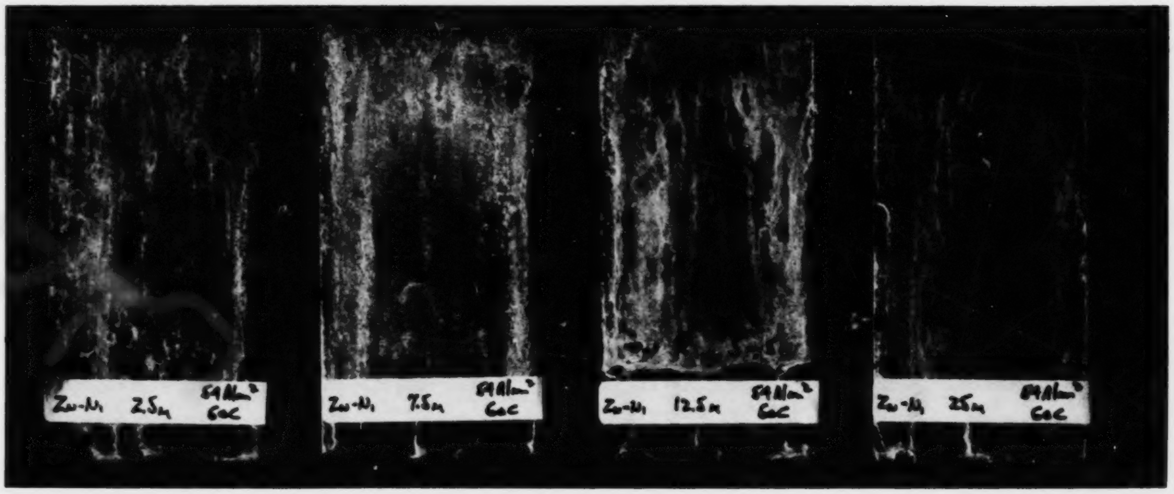
No Chromate Treatment (salt fog exposure time as indicated on panels)



Chromate Treatment (500 hours salt fog exposure)

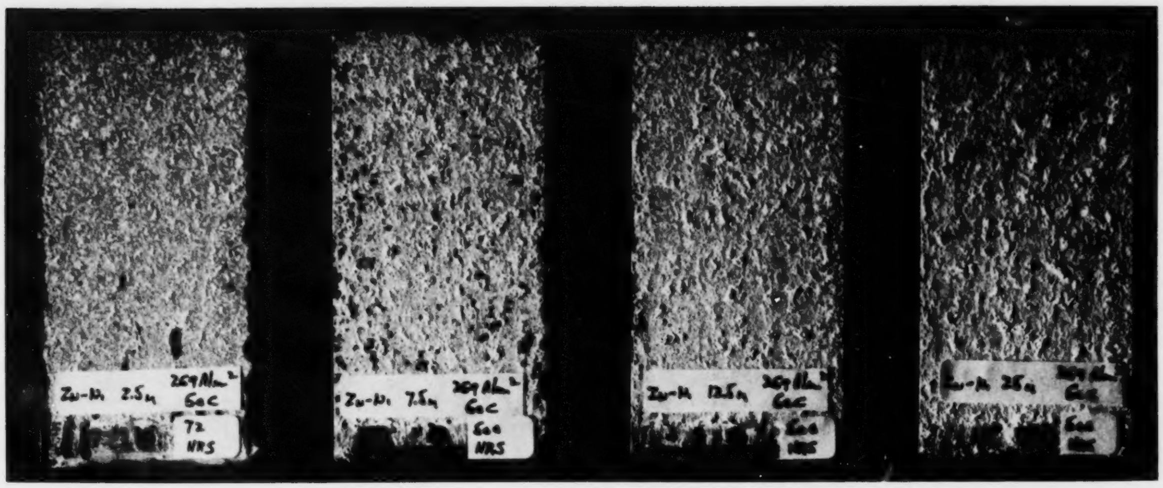


No Chromate Treatment (salt fog exposure time as indicated on panels)

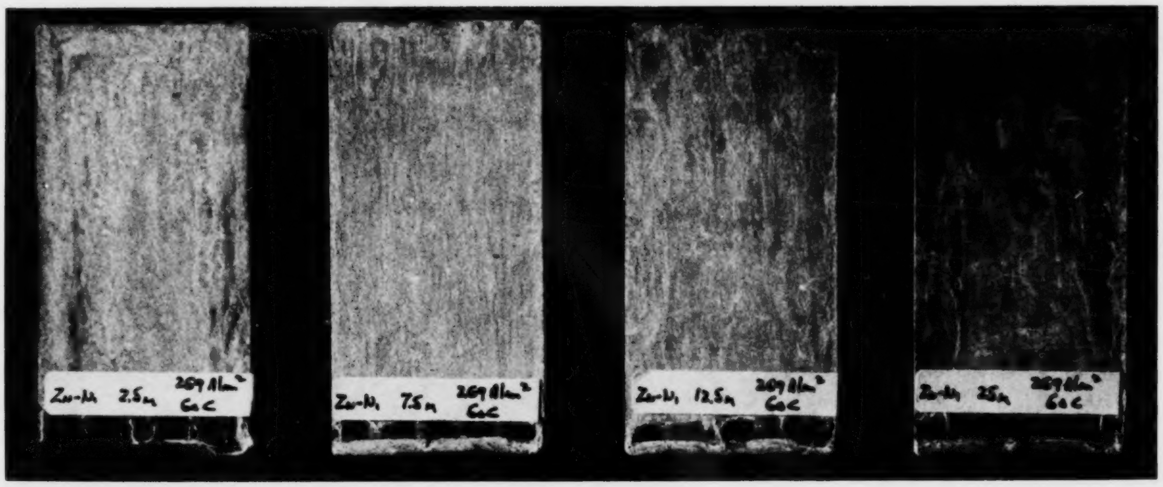


Chromate Treatment (500 hours salt fog exposure)

Dini, Johnson - Figure 10

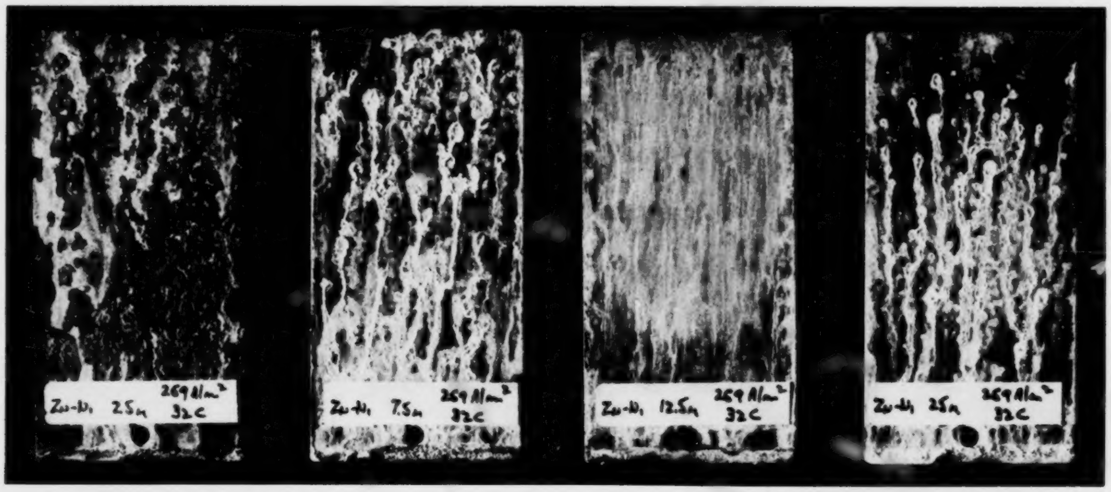

Zn-Ni 2.5μ 269 A/m^2 60C
72 HRS
Zn-Ni 7.5μ 269 A/m^2 60C
600 HRS
Zn-Ni 12.5μ 269 A/m^2 60C
600 HRS
Zn-Ni 25μ 269 A/m^2 60C
600 HRS

No Chromate Treatment (salt fog exposure time as indicated on panels)


Zn-Ni 2.5μ 269 A/m^2 60C
Zn-Ni 7.5μ 269 A/m^2 60C
Zn-Ni 12.5μ 269 A/m^2 60C
Zn-Ni 25μ 269 A/m^2 60C

Chromate Treatment (500 hours salt fog exposure)

Dini, Johnson - Figure 11


Zn-Ni, 2.5μ 259 A/m^2 32C
Zn-Ni, 7.5μ 259 A/m^2 32C
Zn-Ni, 12.5μ 259 A/m^2 32C
Zn-Ni, 25μ 259 A/m^2 32C

Electrodeposition of Zinc-Nickel Alloy Coatings

DISCUSSION PERIOD

MR. GROBIN: Allen Grobin, IBM Corporation.

I think the authors have made a case for the alloy. However, I would like to point out that the use of the salt spray test, ASTM B-117 is being incorrectly interpreted here.

The salt spray test is not a corrosion test. It's a quality control test which is used to show that the plating you did today is equivalent to the plating you did yesterday. It provides no means of comparison between different materials. It represents a five percent salt environment.

MR. LEVY: I would guess that they wanted some standard tests for comparison. I'm sure the point is valid.

MR. GROBIN: I would then suggest that they look at temperature and humidity tests, which appear to be much more representative of the types of corrosion that we see in the United States.

MR. DROSTEN: Fred Drosten, Army Aviation Research and Development Command, St. Louis.

I notice from your slides that the alloy platings most of the time will erupt. Is that just an appearance or was it rough, or is this a crystal structure we are looking at?

MR. LEVY: That's probably a question that will have to be deferred to the authors. It certainly had that appearance, yes.

Alternative Materials and Processes

Session II

Tuesday Afternoon 4:55

CORROSION RESISTANT COATINGS CONTAINING LUBRICATING SOLIDS AS AN ALTERNATIVE TO CADMIUM PLATING

G. R. Kliemann
D. J. Sargent
E/M Lubricants, Inc.
A Subsidiary of
Great Lakes Chemical Corporation
West Lafayette, Indiana 47906

Corrosion resistant coatings containing lubricating solids have been used effectively as an alternate to cadmium plating on fasteners, carburetor parts, electrical connectors, gears, shafts, splines, bushings, bearings, etc. On fasteners, drive torque to clamp loads are maintained. Corrosion resistance is maintained. Costs for these coatings and their application is competitive. These coatings are currently in the market place, and major users are aware of their viability. Comparative data is discussed regarding corrosion resistance, wearability, friction, costs, etc.

CORROSION RESISTANT COATINGS CONTAINING LUBRICATING SOLIDS AS AN ALTERNATIVE TO CADMIUM AND ELECTROPLATINGS ON FASTENERS AND OTHER HARDWARE

Colonel R. Kliemann
Midwestern Regional Manager

E/M LUBRICANTS, INC.
129 Eisenhower Lane South
Lombard, IL 60148

Donald J. Sargent
Vice President-Technical Director
E/M LUBRICANTS, INC.
P. O. Box 2200
West Lafayette, IN 47906

CORROSION RESISTANT COATINGS CONTAINING LUBRICATING SOLIDS AS AN ALTERNATIVE TO CADMIUM AND ELECTROPLATINGS ON FASTENERS AND OTHER HARDWARE

For the past quarter century, the use of solid film lubricants (also referred to as dry film lubricants, bonded solid lubricants, resin bonded lubricants, dry films, bonded coatings, or solid films) has grown substantially. Variations of these coatings have been successfully used on DOD and industrial applications on a wide variety of hardware. A broad range of military and industrial specifications cover many solid film lubricants. Solid lubricant coatings have found utilization in a wide range of applications requiring friction reduction/anti wear, load carrying/anti-galling and corrosion resistance.

Lubricant coatings for such applications (meeting military and industrial specifications) have not found wide acceptance in the fastener industry, however, for a number of reasons:

1) High application costs;
2) Limited corrosion resistance;
3) Torque ranges for coatings containing conventional solid lubricants unpredictable;
4) High processing volumes;
5) Little real technical incentive.

For the past two years, our firm has been engaged in a development program to produce coatings that would meet the needs for the mechanical fastener industry, in a broad sense, as well as serve as a superior substitute for various platings.

A review of the needs for mechanical fasteners disclosed the following basic user criteria:

1) Extended corrosion resistance -
   Especially in the automotive, aircraft, marine and construction industries;
2) Consistent preloading (clamping torque) -
   Standard deviation for preloading of lubricated fasteners is generally less than half that of dry fasteners;

3) Consistent driving torques -
   Driving torque of unlubricated fasteners generally increase and are unpredictable with fastener reuse, causing inaccurate preload on reused fasteners;

4) Reliability -
   Half the "in-place" cost for a fastener results from time to assemble. This promotes automated assembly systems. Lubricated fasteners are more reliable in automated assembly systems;

5) Cleanliness -
   Lubricated fasteners, currently, are essentially of two types:
   a) waxed metallic platings;
   b) oil impregnated conversion coatings.
   Problems common to fasteners of either type are staining of dry wall and fabrics, painting problems, limited shelf life, galling, etc.

6) Environmental impact -
   Many electroplatings are undesirable in terms of effluent pollution.

7) Coating uniformity -
   Uniformity of deposition on threads, thread roots, and heads is important.

Consumer demands, government regulatory requirements, and associated potential liabilities are increasing the need for alternates to current day electroplatings. One such alternative and a very viable one, is the use of solid lubricant containing coatings. Such coatings have been developed and have been evaluated and found, by the fastener industry, to satisfy most fastener industry needs. For example:

1) Torque performance -
   a) prevailing torque to clamp torque ratios are in the range of cad plate and wax;
   b) driving torques are comparable to cad plate and in most cases much narrower in range;
   c) torque is unaffected by lapse time before use;
   d) on-off torque remain relatively stable, assuring

consistent clamping torques for many reuses;

   e) coated self-drilling screws perform well within the three second max drill time specifications.

2) No galling, even on self-drilling/self-threading and deformed locknut applications.

3) Corrosion resistance is a function of a number of factors including part configuration; therefore, it is difficult to give precise and meaningful data in a generalized discussion. We will, however, make some generalized statements:

   a) Using a criteria such as typical phosphated automotive fastener performance, i.e. failure is judged as three rust spots over 1/16 inch in diameter per square inch, on significant surfaces, 48 hours is very achievable for coated fasteners that have been set or driven in place.

   b) 240 hours (on driven fasteners) is achievable at fractionally higher processing and/or coating costs.

   c) 3000 hours have been achieved on hardware, after installation.

Evidence obtained to date indicates that these coatings generally limit rust creep past the initiating spot.

The coatings are still under development department control and are undergoing product improvements; however, we have processed production parts in substantial quantities during the last year.

Many of the large cold headers were introduced to the coatings and are using them in problem solving. Coating variations are under evaluation by several automotive manufacturers and their suppliers. Results are extremely promising. Appliance manufacturers are using the coating in many critical applications.

The applications, while not proprietary or confidential, do involve tradenames and other characteristics that would require formal releases if published. Therefore, we are not listing tradenames or firms. We would be pleased to discuss, on an informal basis, the company names and personnel that could be contacted for user details.

We believe, as do a growing number of people in the fastener industry, that our coatings offer great potential as replacements for electroplate, particularly cadmium plate, on fasteners and other hardware, and we certainly appreciate this opportunity to present our story.

CORROSION RESISTANT COATINGS CONTAINING LUBRICATING SOLIDS

DISCUSSION PERIOD

VOICE: Yes, my question was, what were the materials in the solid lubricant you were talking about, and what are some of the inhibitors that may have been used with them.

MR. SARGENT: I have to respond to your question by saying that is in the realm of propriety, and I'm afraid I can't answer that.

Alternative Materials and Processes

Session III

Wednesday Morning 9:30

ARTIFICIAL SHELLFISH FOR MONITORING AMBIENT CADMIUM LEVELS IN SEAWATER

William B. Kerfoot
Environmental Devices Corporation
Marion, Massachusetts 02738

The adsorption kinetics of artificial oysters (METRO-DISC* TYPE 140) are compared with the accumulation of cadmium by natural populations of shellfish reared in a prototype tertiary treatment-aquaculture system. Accumulation of metal in the aquaculture system was studied with two types of photoplankton, a green platymonad (Prasinocladus tricornutum) and a mixture of diatoms (predominantly Phaeodactylum tricornutum and Chaetocerus simplex), and two species of shellfish, the American oyster (Crassostrea virginica) and the hard clam (Mercanaria mercenaria). The algae showed a rapid increase in metal concentration until an equilibrium was reached, proportional to the initial concentration introduced. Shellfish species exhibited a continual increase in concentration when exposed to seawater and algae mixtures contaminated with cadmium. Separation of the two pathways of transfer identified the algae as a principal source of accumulation in the aquaculture system, while direct adsorption of soluble cadmium was the dominant pathway of accumulation by shellfish in natural waters. Adsorption of the direct pathway can be monitored by laminate discs containing a chelate matrix sandwiched between membrane filters. The discs act like artificial shellfish by integrating ambient metal concentrations with time.

---

*Commercial Name

Preceding page blank

ARTIFICIAL SHELLFISH FOR MONITORING AMBIENT CADMIUM LEVELS IN SEAWATER

William B. Kerfoot
Environmental Devices Corporation
Marion, Massachusetts 02738

ABSTRACT

The absorption kinetics of artificial oysters (METRO-DISC* sensors), are compared with the accumulation of cadmium by natural populations of shellfish reared in a prototype tertiary treatment-aquaculture system. Accumulation of metal in the aquaculture system was studied with two types of phytoplankton, a green platymonad (Prasinocladus tricornutum) and a mixture of diatoms (predominantly Phaeodactylum tricornutum and Chaetocerus simplex), and two species of shellfish, the American oyster (Crassostrea virginica) and the hard clam (Mercenaria mercenaria). The algae showed a rapid increase in metal concentration until an equilibrium was reached, proportional to the initial concentration introduced. Shellfish species exhibited a continual increase in concentration when exposed to seawater and algae mixtures contaminated with cadmium. Separation of the two pathways of transfer identified the algae as a principal source of accumulation in the aquaculture system, while direct absorption of soluble cadmium was the cominant pathway of accumulation by shellfish in natural waters. Absorption via the direct pathway can be monitored by laminate discs containing a chelate matrix sandwiched between membrane filters. The discs act like artificial shellfish by integrating ambient metal concentrations with time.

---

*TM

A need exists for economical and reliable monitoring of heavy metal concentrations in marine environments, particularly to control the rate of exposure of organisms such as shellfish during aquaculture operations and to control rates of corrosion at a source. Pringle et.al. (1968) found that soft shell clams accumulated cadmium at a rate of 0.1 ug/g wet weight/day. Kerfoot and Jacobs (1976) studied the food-chain mechanics of accumulation of cadmium and defined a linear regression between dissolved cadmium and the rate of accumulation in shellfish. Rossenburg (1967) employed the natural concentrating ability of oysters to investigate copper erosion and leaching from power plant condenser tubes. The following text compares the observed absorption mechanics of live shellfish to the uptake of artificial oysters designed for monitoring.

Live organisms respond to background metal levels through different mechanisms, reacting to particulate loadings in a manner distinct from dissolved forms. The mechanics of concentration can be quantified for individuals and populations to provide a valuable tool for measuring dosage. However, the reliance upon live organisms introduces several inherent difficulties into interpretation of background metal concentrations (Brainard and Kerfoot 1975). Frequent problems are often due to:

1. The difficulty of maintaining healthy shellfish populations when exposed to a variety of environmental and discharge conditions.

2. Individual variability in uptake based upon physiological conditions, age, and temperature.
3. Seasonal variability in whole body metal concentration due to spawning activities.
4. Weight loss of body fluids during thawing or cleaving.
5. The need for expensive chemical digestion and sample preparation.

ABSORPTION KINETICS OF SHELLFISH.

The uptake of cadmium by shellfish was intensively investigated in flowing aquaculture systems employed in a prototype tertiary treatment-aquaculture system in operation at Woods Hole Oceanographic Institution. (Kerfoot and Jacobs, 1976). In the study, two species of algae and two species of shellfish, under cultivation in the treatment-aquaculture system, were exposed to cadmium. One algae culture was dominated by a green platymonad, Prasinocladus subsadsa, the other by a mixture of diatoms, predominantly Phaeodactylum tricornutum and Chaetocerus simples. The diatoms are the normally preferred food since they encourage rapid growth during culture. The green algae, which are considered undersirable from a culture standpoint, commonly coat the sides of culture pools and replace the diatoms unless the tanks are cleaned frequently. The American oyster (Crassostrea virginica) and the hard clam (Mercenaria mercenaria) were the shellfish species employed in this study. The oysters were obtained from Long Island Oyster Farms, Inc., and the clams removed from beds seaward of Chatham, Massachusetts.

Phytoplankton was cultured by batch exposure in media specially prepared from Guillard and Ryther's "f". A started monoculture of 100 ml of algae was added to the media, and the mixture brought to a final volume of 2 liters. In enrichment experiments, a 1000 ppm standard of Cd^{2+} in doubly-distilled water was prepared from cadmium iodide salt (CdI_2) before dilution with seawater. Then 5 ml of cadmium stock solution, diluted to yeild the appropriate concentration, was added to the solution. Batched cultures of the algae were placed under fluorescent lights and agitated continually by magnetic stirring bars at 20°C. Harvested phytoplankton was collected on acid-rinsed membrane filters (3 μ Nuclepore), rinsed with distilled water, dried, wet-ashed, and analyzed for total content of cadmium.

For direct exposure of shellfish, the stock cadmium solution was diluted by seawater up to 10.1. The resulting cadmium solution was then mixed at a rate of 7-300 ml/min of seawater before flowing into 40 x 60 cm fiberglass trays containing oysters and quahogs. The controlled residence time in the tray was 22 minutes. A control tray received only seawater and phytophankton as food. At each sampling period, three shellfish were removed, allowed to void their intestinal tracts by placing the animals in clean seawater for 1 hour, and then frozen.

To determine the transfer through ingestion, phytoplankton exposed to Cd was resuspended in uncontaminated seawater, fed to shellfish, and then the shellfish were analyzed for accumulation. Algae were cultured in 10-l. carboys enriched with cadmium as previously described. Samples were taken to measure carbon, nitrogen, and hydrogen composition.

After 5-day exposure, sufficient to establish equilibria, the algae were removed from solution by continuous centrifuging and then resuspended in 100 ml of uncontaminated seawater. Microscopic examination of a 1-ml aliquot was made following centrifugation to assure that cells were not damaged during removal and resuspension. A second sample of 10 ml was removed for analysis of total cadmium and concentration on a dry weight basis.

Shellfish were fed the contaminated algae by two methods: the resuspended algae were diluted to 10-l., placed in a 12-l. carboy, and added continuously during 24 hours to a tray containing shellfish; or apportioned to 500 ml of seawater in 1-l. beakers holding individual shellfish. Periodic sampling of the water was performed to monitor changes in the dissolved cadmium concentration. After a set time or, in the case of individual feeding, when the suspended algae were removed from solution, the shellfish were placed in uncontaminated flowing seawater to allow time to completely void their tracts of ingested matter. The specimens were then frozen prior to digestion and analysis.

For wet ashing, the entire body of an oyster or clam was removed from the shell, rinsed with distilled water, weighed, and transferred to a aqua-regia washed 125-ml Erlenmeyer flasks. Phytoplankton was rinsed with distilled water, dried in a warming oven at 50°C for 24 hours, weighed, and added to similar acid-rinsed flasks. A detailed description of the digestion and analytic procedure can be found in Kerfoot and Jacobs (1976). All analyses were done on a Jarrell-Ash Model 800 atomic absorption spectrometer, a double-beam dual-channel instrument with recorder printout.

Algae were ashed and analyzed following the same procedure as shellfish.

PHYTOPLANKTON UPTAKE OF CADMIUM.

Figure 1 illustrates uptake observed in a 0.05 µg/ml (ppm) solutions of cadmium simulating the algal culture tanks. Cadmium was incorporated rather rapidly during the first few hours of exposure and then at a progressively diminishing rate. After 24 hours a roughly constant level of cadmium concentration was reached in the cultures.

Samples of batches removed 5 days following addition of cadmium showed a proportional increase in the content of cells with increase in concentration in seawater (Figure 2). The green platymonad, *Prasinocladus subsalsa*, showed a greater tendency to accumulate cadmium than the mixed diatom culture of *Phaeodactylum* and *Chaetoceros.*

SHELLFISH UPTAKE OF CADMIUM FROM SEAWATER.

Both oysters and clams responded to cadmium enrichment of seawater with a linear accumulation of metal in their tissues for the entire duration of an experiment and over all concentration ranges studied (Figure 3). Originally, the oysters (*Crassostrea virginica*) and the clams (*Mercenaria mercenaria*) contained background concentrations of 1.77 ± 0.29 and 0.09 ± 0.02 µg/g (ppm) wet weight of tissue, respectively. Each point in Figure 3 represents the mean of three individual shellfish analyses. The rate of accumulation varied with concentration, the higher the level of cadmium in seawater the greater the rate of uptake. The addition of 0.03 µg/ml (ppm) cadmium was continued for 67 days without any apparent departure from linearity. No mortality of shellfish that could be related to metal poisoning was recorded with experimental animals at any concentration being studied. After 17-day continuous exposure to seawater containing cadmium, no further metal was added to the 0.05 ppm system. The shellfish were allowed to stand in running seawater for 25 days. Analyses of the oyster during this time showed no measurable decrease in cadmium content of the tissue (Figure 3).

SHELLFISH UPTAKE VIA INGESTION OF DIATOMS.

Early in the investigations of phytoplankton uptake, algae exposed to cadmium could be resuspended in uncontaminated seawater and would retain their original cadmium content for a considerable time. The algae were removed from solution by continuous centrifuging and then resuspended in 100 ml of uncontaminated seawater. A second sample of 10 ml was removed for analysis of cadmium concentration per dry weight of tissue and total content per ml of algae. Shellfish were then fed the contaminated algae by two techniques: the resuspended algae were placed in a 10.1. carboy with seawater and added daily to a tray containing shellfish; or apportioned 10 or 20 ml resuspended algae to 500 ml seawater in 1-1. beakers holding individual oysters.

In general, the shellfish assimilated little of the cadmium presented to them in the algal diet (Table 1). The percentage of cadmium persisting following feeding was calculated only when a significant difference was detected between controls and experiments.

Table 1. Uptake of Cadmium from Ingested Algae

Organism	Number of Individuals	Mean Weight (meat)	Total µg Cd Fed in Algae	Final Cd Content (ppm wet weight)	Significance	% Uptake
			Prasinocladus - Batch Exposure			
Oyster	4	3.29	1.1	1.91 ± .25		
	5	3.41	67.5	2.63 ± .42	p < .025	7.3%
			Prasinocladus - Continuous Exposure			
Oyster	4	4.37	0	1.77 ± .25		
	16	3.82	41.6	3.25 ± .43	p < .02	14.3%
Clam	7	5.95	0	.08 ± .014		
	4	6.59	41.6	.48 ± .18	p < .01	7.0%
			Phaeodactylum-*Chaetoceros* - Batch Exposure			
Oyster	10	7.52	0	1.23 ± .20		
	5	5.38	92.5	3.58 ± .77	p < .01	13.6%
	2	7.86	109.0	2.38 ± .38	p < .01	4.7%
Clam	11	8.63	0	.21 ± .04		
	4	10.40	10.4	.15 ± .02	ns	
	2	8.73	92.5	1.18 ± .31	p < .01	9.1%

Crassostrea retained from 4.7 to 14.3% of the total cadmium fed in the food, with hardly a noticeable difference between species of algae. Similarly, *Mercenaria* removed 7.0 and 9.1% of the cadmium presented it in the separate diets of the green algal and diatom species, respectively. If the natural seawater is enriched with cadmium, the greatest load of metal is obtained directly through absorption.

To demonstrate the difference, in Figure 4, the expected rate of increase in cadmium content of tissue is compared for 3-g oysters and 5-g clams under natural coastal seawater conditions. For instance, a 3-g oyster commonly ingests 1.4 mg of carbon per day derived from coastal seawater. When feeding on *Prasinocladus*, which has a measured carbon content of 26.3% dry weight, the intake amounts to 0.0053 g dry weight of algae per day. Exposed to 0.10 μg/ml (ppm) cadmium in the seawater, the algae would contain 670 μg cadmium/g dry weight. Using the highest retention measured (14.3%), each day a feeding oyster would ingest 3.55 μg of cadmium with only 0.5 μg being retained. Diffused throughout the 3-g weight of the oyster, the projected increase in cadmium content of the tissue would be 0.16 μg cadmium/g day from ingested algae (as indicated by the line marked "OYSTERS--Ingestion" on the left hand of Figure 4). Even considering the algae which absorb cadmium the highest and using the greatest measured percent retention, we note ingestion of contaminated algae (by the oysters) under natural seawater conditions contributes only about 1/10 of that absorbed directly from solution.

ARTIFICIAL SHELLFISH FOR MONITORING MARINE WATERS.

While posing inherent problems, shellfish do possess an important ability to remove metallic ions from solution, integrate time effects, and concentrate the ions internally to high levels, reflecting ambient concentrations in background water. The difficulties created by employing live organisms may be overcome by developing mechanical analogs which incorporate the desirable attributes of shellfish while eliminating the detrimental characteristics. Environmental Devices Corporation has been developing an artificial shellfish for the past 5 years. The first analog device was termed the METRO-DISC[+] Type 140 sensor.

Design.

The fabricated shellfish includes a layer of an adsorptive material sandwiched between a pair of porous membranes (Figure 5). The adsorptive agent consists of ENDECO[*] Type 140 chelate exchange matrix engineered for this specific application. Hydrophilic polycarbonate membranes are used and have a degree of porosity selected to regulate the uptake of soluble metal by the adsorptive matrix. The two membranes are heat sealed to a spacer ring placed around the inner circumference of the disc.

When the METRO DISC is placed into aqueous solution, metallic ions diffuse through the membranes and are adsorbed linearly with time to the chelate matrix (Figure 5). The porous membrane barrier reduces the usual rapid uptake found with the freely suspended adsorptive matrix to below .4% of the total content in solution

[*] Reg.U.S.Pat.Off.
[+] TM

per 24 hours, or with copper (Cu^{2+}) to 4.0 µg per 24 hour period in a solution containing 1000 µg per liter. Restricting adsorption to a small percentage of the total solute avoids competitive interactions among ions which would interfere with independent adsorption. With 10 µg of adsorptive material, the adsorbed 4.0 µg of copper represents a concentration by weight which is 400 times the background concentration of Cu (1000 µg/kg) in solution. The amount of metal adsorbed is relatively independent of the weight of adsorptive agent used (Figure 5), allowing the mass to be varied to obtain the range of concentration desired on the adsorptive agent for analysis by combustion. For analysis by atomic emission a minimum of 4 µg is desirable, yielding a maximum concentration factor for Cu^{2+} of 1000 times background concentration.

The uptake of metal by the METRO-DISC sensor can be described by the formulation:

$$C_m = \frac{at}{M} C^b$$

where: C_m = the concentration on the adsorptive matrix (µg/mg)

C = the concentration in solution (µg/liter)

M = the mass of adsorptive material (mg)

t = time (in hours)

a = the rate of uptake in hours (µg/hr)

b = slope of activity of adsorption

By combining the appropriate chelating agent with the correct membrane, the METRO-DISC sensor can be designed to collect specific metals at definite or definable rates.

The sensitivity of uptake to temperature was also investigated. The 24-hour adsorption of copper was obtained in distilled water solution at temperature extremes of 3°C and 24°C. The results are plotted on log-log coordinates in Figure 5. A combination of the membrane porosity and chelation reaction significantly reduces the sensitivity to temperature.

The Type 140 METRO-DISC sensor removed ions from solution by passive diffusion and locked the capacity to record the precise volume of water extracted and the particulate metal concentration in the sampled water. Most recently Environmental Devices Corporation has developed the Type 1410 METRO-DISC ion filter which can be used with prefilters for precision monitoring of particulate and dissolved transition metals, particularly cadmium (Kerfoot and Crawford, 1977).

Seawater aliquots of 200 ml each were placed in 250-ml acid-rinsed pyrex glass beakers and gently mixed by rotation. Type 1410 METRO-DISC sensors were mounted in in-line filter holders sequentially placed in a 5-sample vacuum manifold (ENDECO Type 886). Simultaneous multi-metal analyses were performed on a Jarrell-Ash Inductively-Coupled Plasma Spectrometer Model 90-975 containing a built-in computer-controlled system for data calibration and statistical manipulation. Reproducibility was also compared by determination by EPA standard methods (EPA, 1974) on a Perkin-Elmer 306 Atomic Spectrophotometer with an HGA 2100 graphite furnace. The calibration series used Eppendorf micropopettes of 1000, 500, 250, 100, 50, and 25 microliters with disposable tips.

Doubly-distilled deionized water was used to wash out interstitial seawater remaining in the METRO-DISC sensor before acid elution. Low metal "Ultrex" nitric acid (Baker) was diluted to a 1% solution for elution of the METRO-DISC sensors. The METRO-DISC sensors were extracted a second time with another rinse of 1% HNO_3 to determine the remaining fraction of acid-leachable metal. Figure 6 shows the concentration of cadmium found in 5 ml of acid elute compared with the original concentration of cadmium added to the background Vineyard Sound seawater. A regression analysis of the methods of additions indicated a detection limit of 0.1 μg/liter with $\pm$11% standard deviation at the 10 μg/l level.

DISCUSSION.

A developing oyster of about 3 grams wet weight will maintain a daily pumping rate of about 10 to 30 liters, depending upon the mass of algae present in the seawater and the ambient temperature. A total intake of 1.3 mg per day is sufficient to maintain the young shellfish (Ken Tenore, personal communication). If 10 liters is processed per day, a retention rate of .45% would be necessary to provide the observed daily rate of cadmium increase of .15 μg/gm wet weight of tissue in a 3-gram oyster. The Type 140 METRO-DISC sensor which adsorbs soluble cadmium passively from solution has an inherent efficiency of extraction identical to that observed from intermittently pumping natural oysters. The rate of increase of the Type 140 is about 10 times greater than the oyster because of the high surface to volume relationship and adsorbtive capacity of the interior matrix. In comparison, when seawater is filtered through a 4 micron prefilter for particulates and passed through the Type 1410 METRO-DISC sensor, an efficiency of extraction of 65% is obtained with an intermittent pumping of 1 liter/day (.042 liters/hr at hourly intervals). The added efficiency of extraction and flow-through arrangement increases the rate of accumulation of metal per unit mass to 1000 times that observed with natural oysters. The Type 1410 can, therefore, be used for daily-monitoring of background natural cadmium.

TABLE 2.

Observed Update of Natural Oysters (3 gm) and Artificial Shellfish Exposured to a Cadmium Concentration of 10 ug/l - ppb in Seawater

Accumulation	Observed Oysters	METRO-DISC 140	METRO-DISC 1410
Weight	Intermittant Pumping 3 gm wet wt.	Continual Exposure 30 mg	Intermittant Pumping (1 liter/day) 30 mg
Rate of Increase ug/gm/day	.15	1.33	220
Efficiency of Extraction	.45%	.4%	65%
Particulate Filtering mg/day	1.4	--	1.0

Concentrations, whereas both natural oysters and the Type 140 METRO-DISC must be left in for at least 10 days to integrate sufficient cadmium to provide a large enough signal to noise ratio for discriminating the daily rate of increase.

Figure Captions

Figure 1. Uptake of cadmium by phytoplankton during culturing.

Figure 2. Content of cadmium in tissue of algae removed after average of 5 days culture.

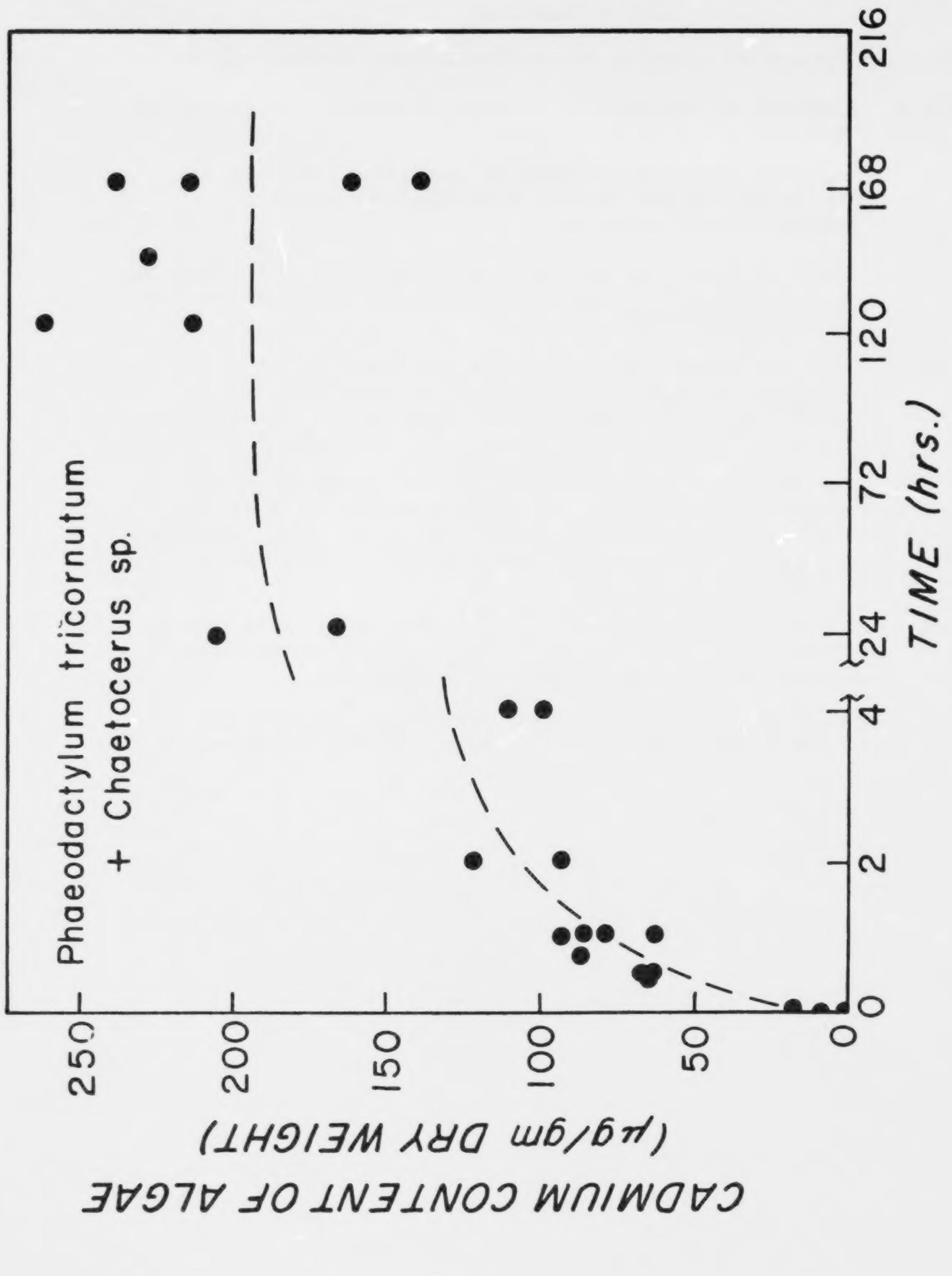
Figure 3. Cadmium content of meat of shellfish removed at different times during continual exposure to contaminated seawater.

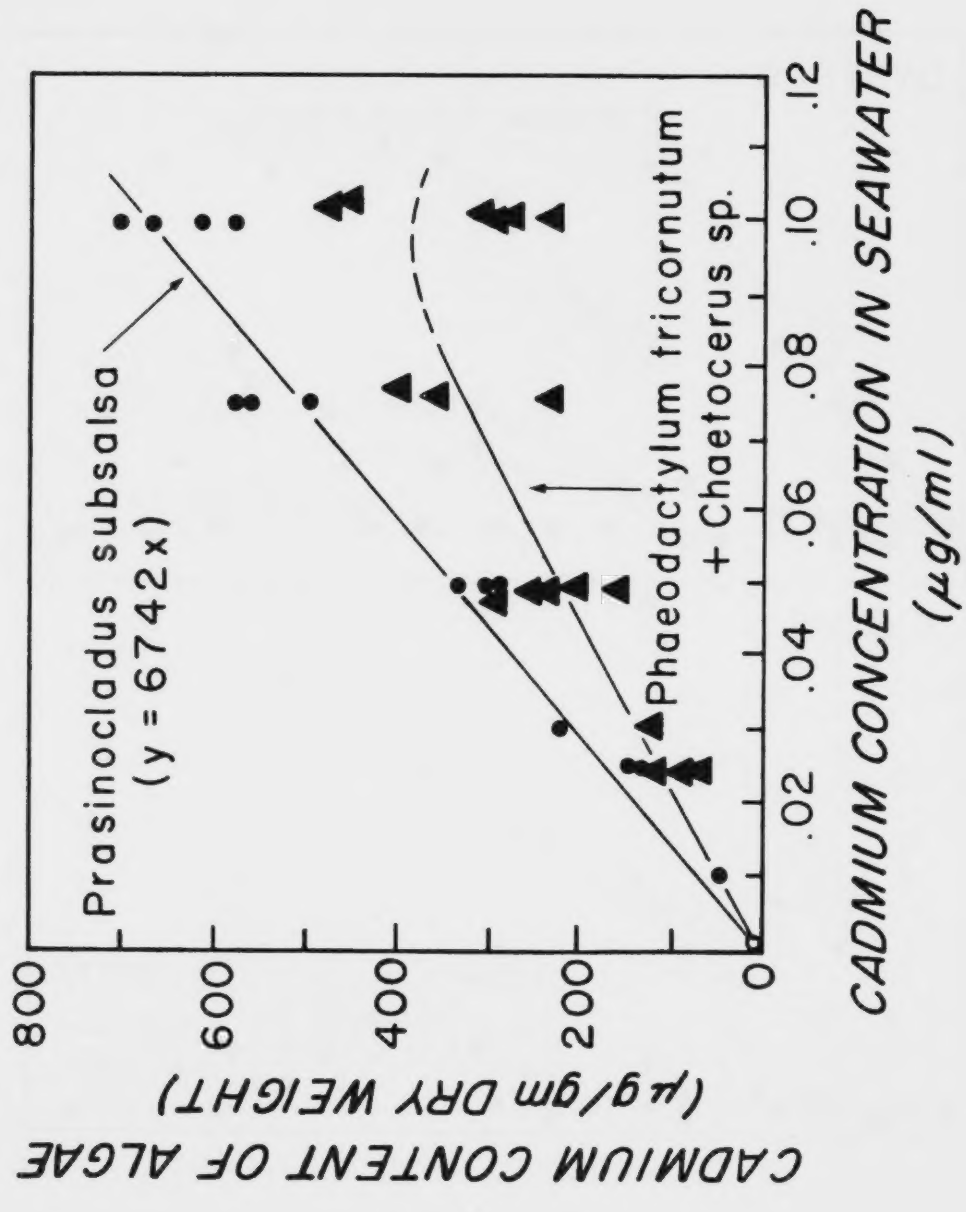
Figure 4. Rate of increase of cadmium in meat of shellfish as a function of concentration in seawater and source of contamination.

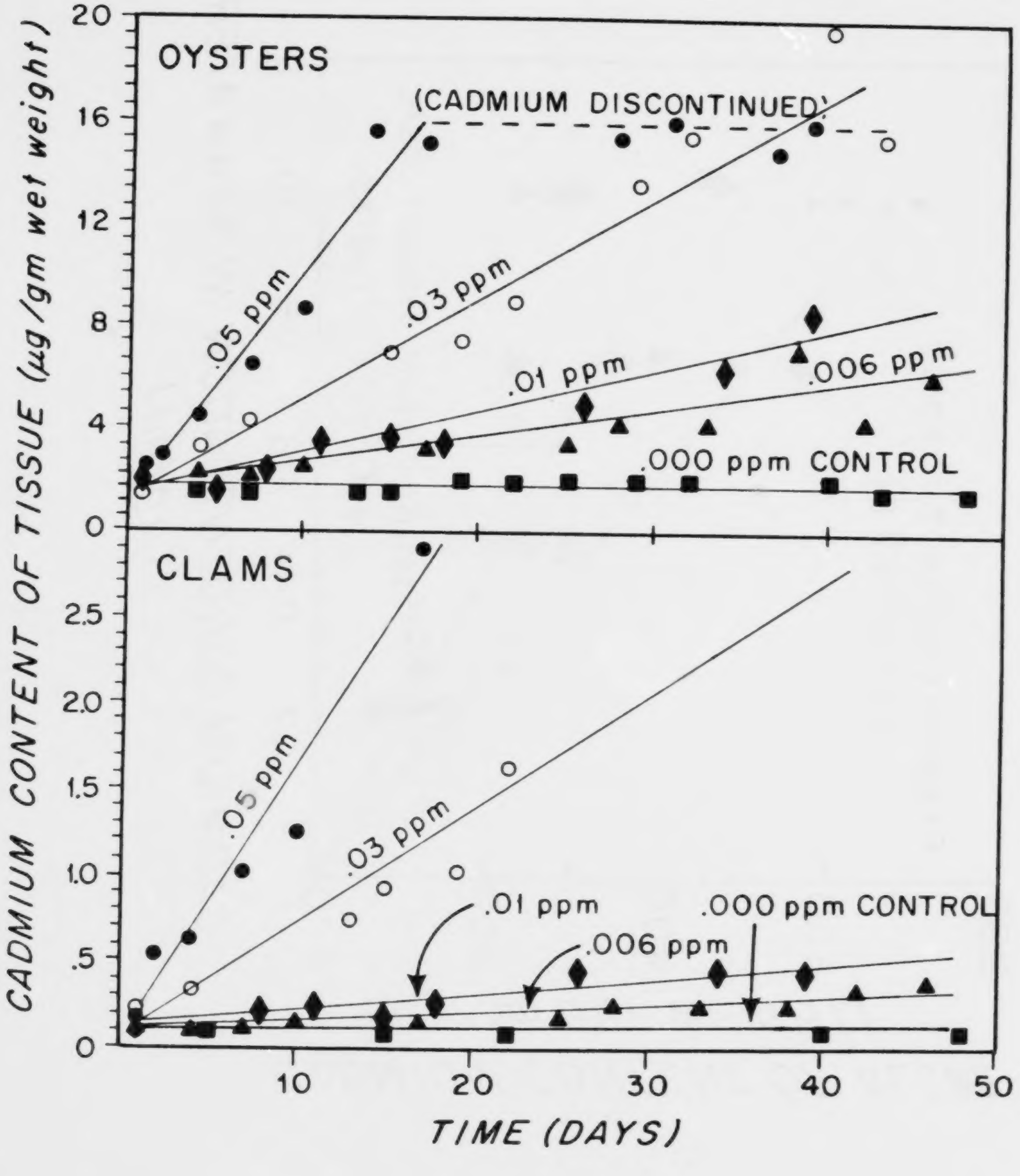
Figure 5. The artificial shellfish is composed of an adsorptive matrix sandwiched between porous membranes (A). The rate of adsorption of copper by the Metro-disc 140 sensor is shown as a function of concentration in solution (B). Using nickel as an example, the concentration of adsorbed metal is shown as a function of concentration in solution and mass of adsorptive material (C). The influence of temperature on 24-hour adsorption uptake of copper (D).

Figure 6. Concentration of cadmium in acid elute from the Metro-disc 1410 sensor as a function of initial concentration of cadmium in seawater.

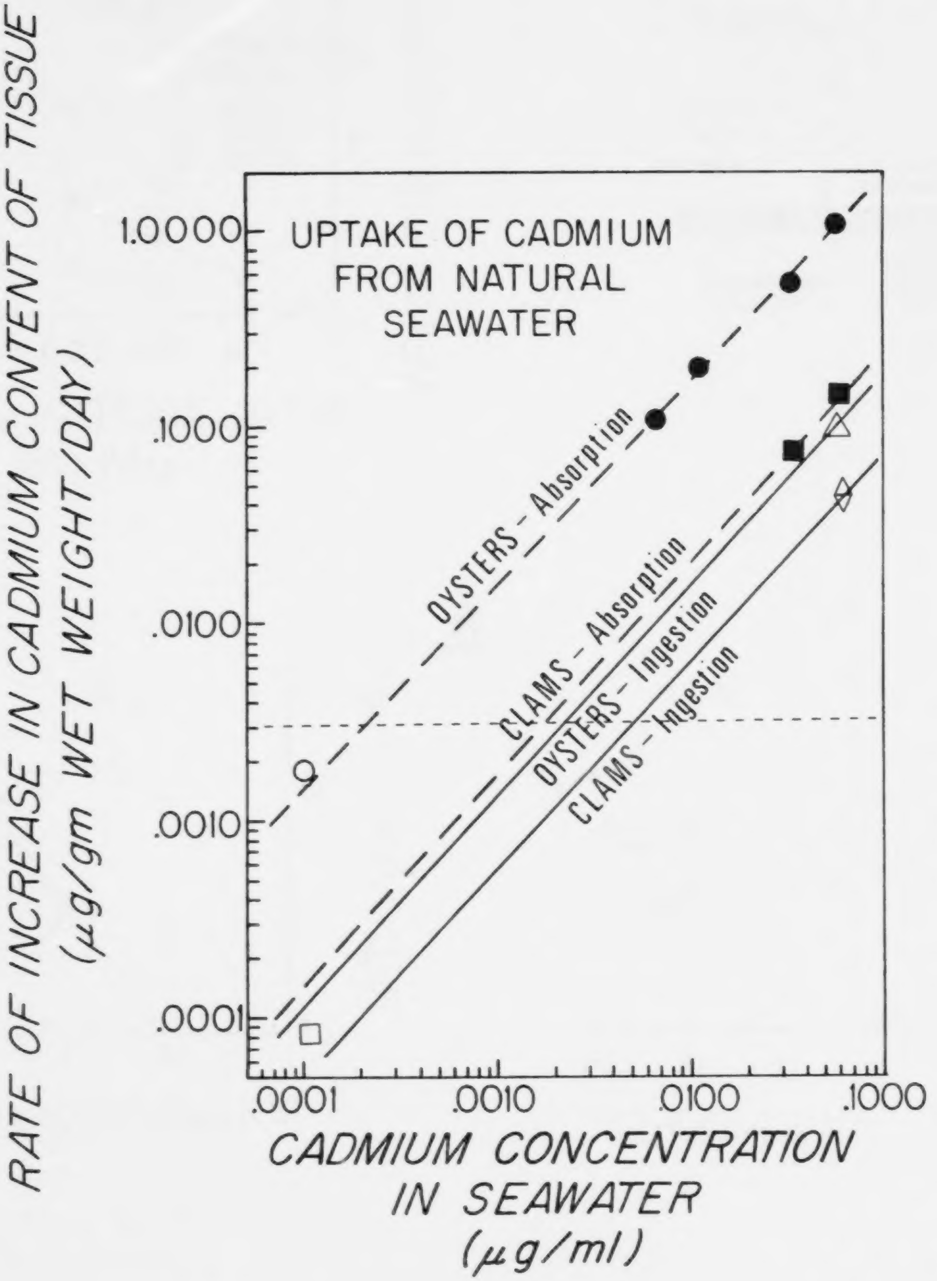
Figure 7. Removal of the .4 micron prefilter (a) and the type 1410 Metro-disc (b) from plastic holders.

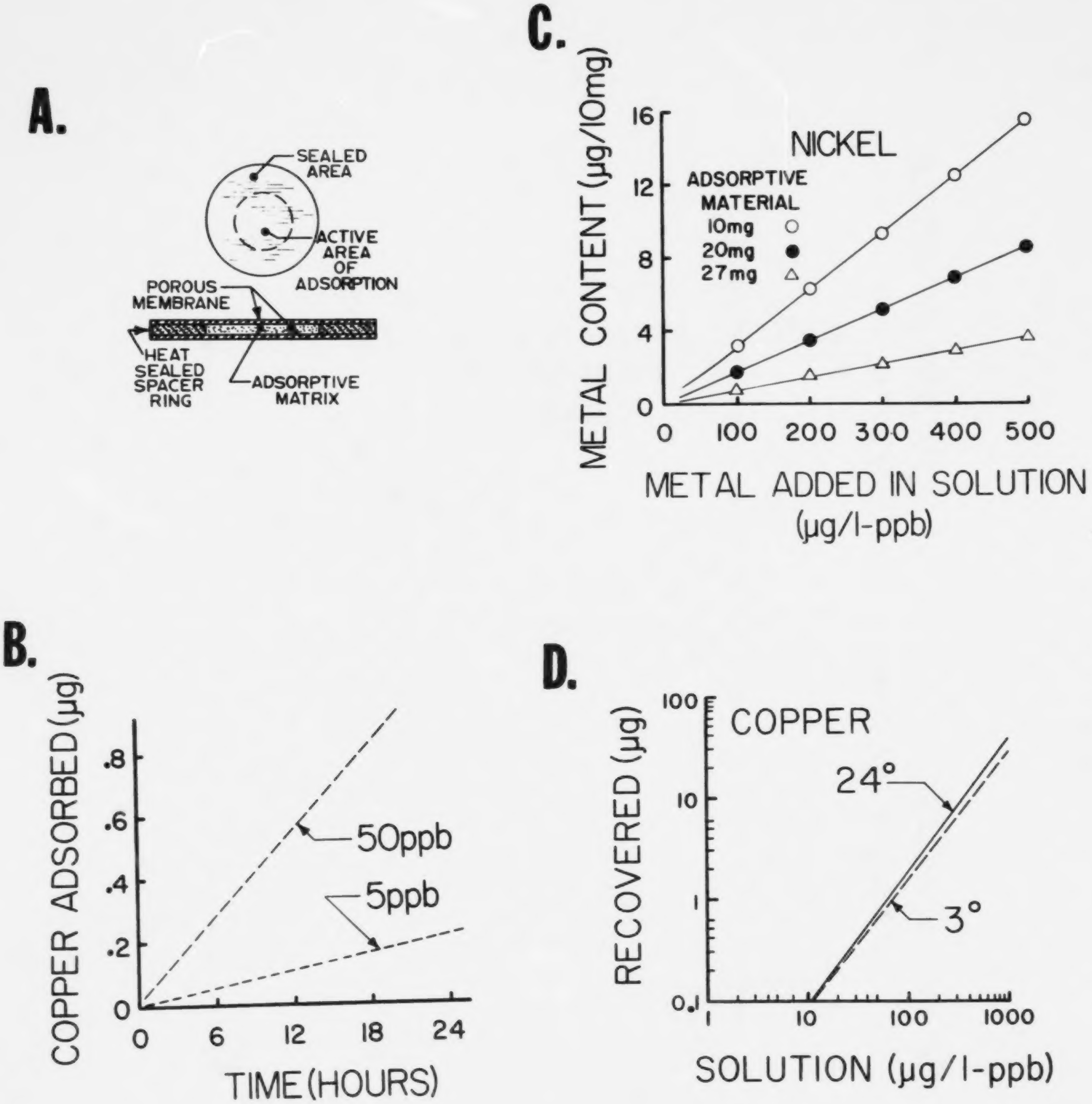

Phaeodactylum tricornutum
+ Chaetocerus sp.
CADMIUM CONTENT OF ALGAE
(µg/gm DRY WEIGHT)
250
200
150
100
50
0
0
2
4
24
72
120
168
216
TIME (hrs.)

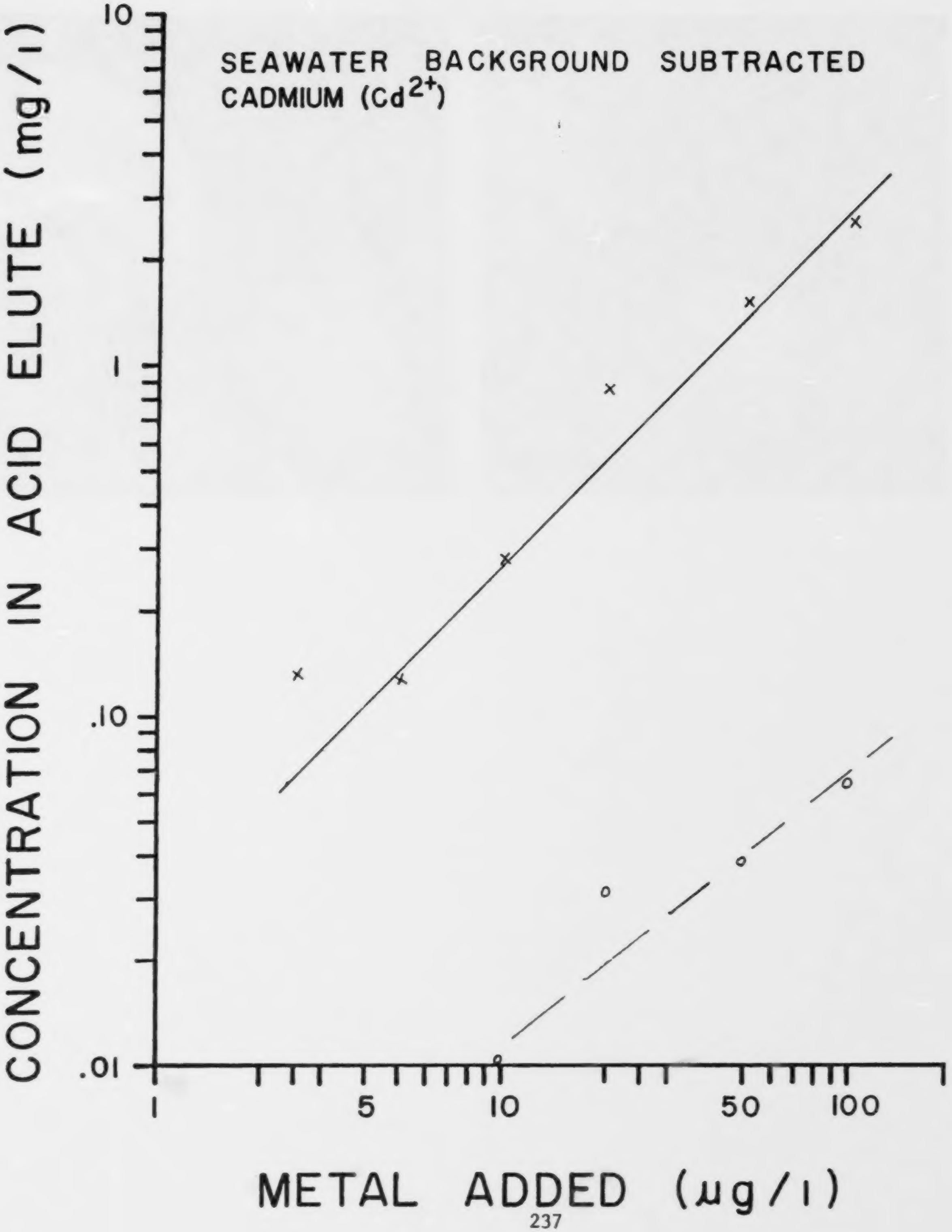

CADMIUM CONTENT OF ALGAE
(µg/gm DRY WEIGHT)
0
200
400
600
800
0
.02
.04
.06
.08
.10
.12
CADMIUM CONCENTRATION IN SEAWATER
(µg/ml)
Prasinocladus subsalsa
(y = 6742 x)
Phaeodactylum tricornutum
+ Chaetocerus sp.

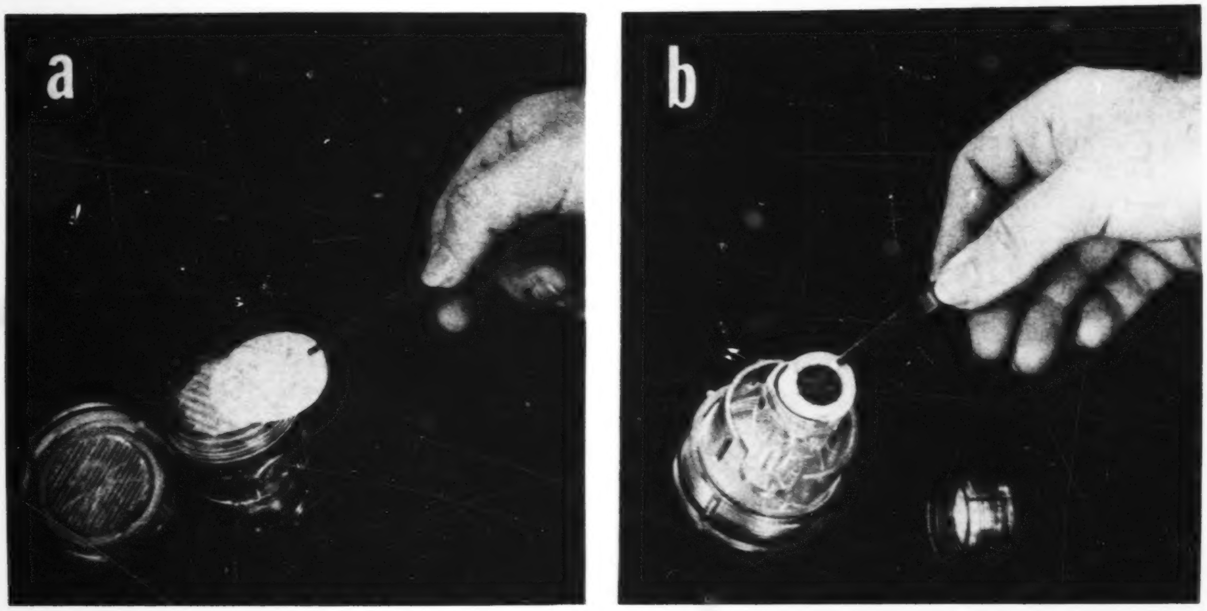


OYSTERS
(CADMIUM DISCONTINUED)
.05 ppm
.03 ppm
.01 ppm
.006 ppm
.000 ppm CONTROL
CLAMS
.05 ppm
.03 ppm
.01 ppm
.006 ppm
.000 ppm CONTROL
CADMIUM CONTENT OF TISSUE (μg/gm wet weight)
TIME (DAYS)
0
4
8
12
16
20
.5
1.0
1.5
2.0
2.5
10
20
30
40
50


UPTAKE OF CADMIUM
FROM NATURAL
SEAWATER
RATE OF INCREASE IN CADMIUM CONTENT OF TISSUE
(μg/gm WET WEIGHT/DAY)
1.0000
.1000
.0100
.0010
.0001
OYSTERS - Absorption
CLAMS - Absorption
OYSTERS - Ingestion
CLAMS - Ingestion
.0001
.0010
.0100
.1000
CADMIUM CONCENTRATION
IN SEAWATER
(μg/ml)


A.
SEALED AREA
ACTIVE AREA OF ADSORPTION
POROUS MEMBRANE
HEAT SEALED SPACER RING
ADSORPTIVE MATRIX
B.
COPPER ADSORBED (µg)
0
.2
.4
.6
.8
50ppb
5ppb
0
6
12
18
24
TIME (HOURS)
C.
NICKEL
METAL CONTENT (µg/10mg)
0
4
8
12
16
ADSORPTIVE MATERIAL
10mg ○
20mg ●
27mg △
0
100
200
300
400
500
METAL ADDED IN SOLUTION (µg/l-ppb)
D.
COPPER
RECOVERED (µg)
0.1
1
10
100
24°
3°
1
10
100
1000
SOLUTION (µg/l-ppb)


SEAWATER BACKGROUND SUBTRACTED
CADMIUM (Cd^{2+})
CONCENTRATION IN ACID ELUTE (mg/l)
10
1
.10
.01
1
5
10
50
100
METAL ADDED (µg/l)


a
b

References

Brainard, E. C. and W. B. Kerfoot, 1975. Artificial shellfish for the extraction and determination of transition metals in aqueous solution. Proc. Marine Technol. Soc. IEEE Ocean, p. 901-905.

E.P.A, 1974. Methods for chemical analysis of water and wastes. National Environmental Research Center, U.S.E.P.A., Cincinnati, Ohio.

Kerfoot, W. B. and R. Crawford, 1977. Rapid multielement analysis of trace metals in seawater by a laminate membrane adsorptive disc for inductively coupled plasma atomic emission spectroscopy. ICP Information Newsletter, 2(10):289.

Kerfoot, W. B. and S. A. Jacobs, 1976. Cadmium accrual in combined wastewater treatment-aquaculture system. Envir. Sci. and Technol., 10:662.

Pringle, B. M., P. E. Hissong, E. L. Katz, and S. T. Mulawka, 1968. Trace metal accumulation by estuarine mollusks. J. Sanit. Eng., 3:455.

Rossenburg, W. H., 1969. Greening and copper accumulation in the American oyster, Crassostrea virginica, in the vicinity of a steam electric generating station. Ches. Sci., 10(3):241.

Artificial Shellfish for Monitoring Ambient Cadmium Levels in Seawater

MR. WHITE: Martin White, Cadmium Association. I am impressed with this very adequate technique. Could you comment on the methods of analysis you used for cadmium in seawater since you are getting to some extremely low levels?

Second, could you comment on the effects of pH and salinity on the performance of your artificial oysters, because often these are used in estuary conditions where there might be tremendous flucuations in salinity over the course of a day?

MR. KERFOOT: On the first question, at that time, we were underway at Wood's Hole Oceanographic with a standard seawater geosect program where we used APDC followed by MIBK solvent extraction procedures to confirm the cadmium concentrations for background levels in the flowing seawater system. We used essentially a standard procedure developed by Derrick Spencer and Peter Brewer at Wood's Hole Oceanographic, certainly in its application to seawater.

In response to the second question, we do find a small decrease in uptake due to salinity and some competition for the chelator sites. This tends to vary, though, over a long exposure period when the principal uptake is by the chelator system on the interior matrix.

This is far superior, in terms of absorptive characteristics because it relies on a chelate-base substrate instead of an ion-exchange substrate. As a result, you do not have the replacement to the extent that you have seen on other products like those which involved Chelax-100 on the surface and deal with very short term ion-exchange reactions.

MR. JORCZYK: Ed Jorczyk, 3M Company. I have seen a lot of oysters come out of the Hoosatonik River in Connecticut which is probably quite heavily contaminated with metal, and I was wondering whether these absorbed metals will color the flesh of the oyster.

MR. KERFOOT: Some metals will. Copper particularly, as noted by Rosenberg, causes an aquamarine blue to occur in the protein structure of the oyster itself.

Alternative Materials and Processes

Session III

Wednesday Morning 10:05

UNIQUE CHARACTERISTICS OF CADMIUM ELECTROPLATING

Albert R. Cook
International Lead Zinc Research Organization, Inc.
Manager, Electrochemistry
New York, New York 10017

Cadmium electroplating need not be a threat to the environment. Available technology can ensure complete safety in processing and in application.

The choice of cadmium plating can thus be based upon rational economic and technical considerations.

The special characteristics of cadmium plating are described.

Case histories are presented to demonstrate the value of cadmium plating in specific applications, especially those where engineering safety factors are of special importance.

Government and industry specifications which involve cadmium plating are cited and possible alternatives are discussed, together with the evaluation procedures which must be followed to prove that substitution can safely be made.

The special needs of the aircraft industry are taken into account.

UNIQUE CHARACTERISTICS

OF CADMIUM ELECTROPLATING

by

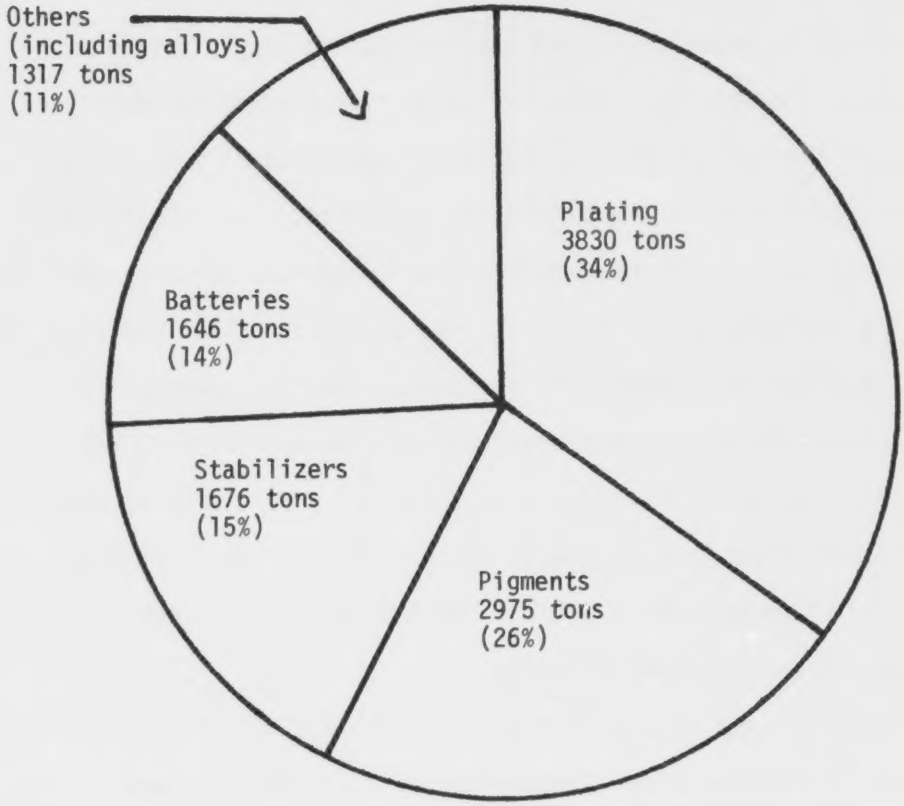
Albert R. Cook
Manager, Electrochemistry
International Lead Zinc Research
Organization, Inc.
292 Madison Avenue
New York, New York 10017

Presented at the U.S. Government-Industry Workshop "Alternatives for Cadmium Electroplating in Metal Finishing", October 4-6, 1977, National Bureau of Standards, Gaithersburg, Maryland.

Cadmium metal, a byproduct of zinc production, is of vital importance to industry.

The end uses of cadmium for five major industrial nations* in 1974 are shown in this pie chart in metric tons(1).

1974 Total: 11444 metric tons



These 3,830 tons of cadmium used for electroplating would be sufficient to provide corrosion protection for 700 million sq. ft. of steel.

* Germany F.R., Japan, United Kingdom, United States and France.

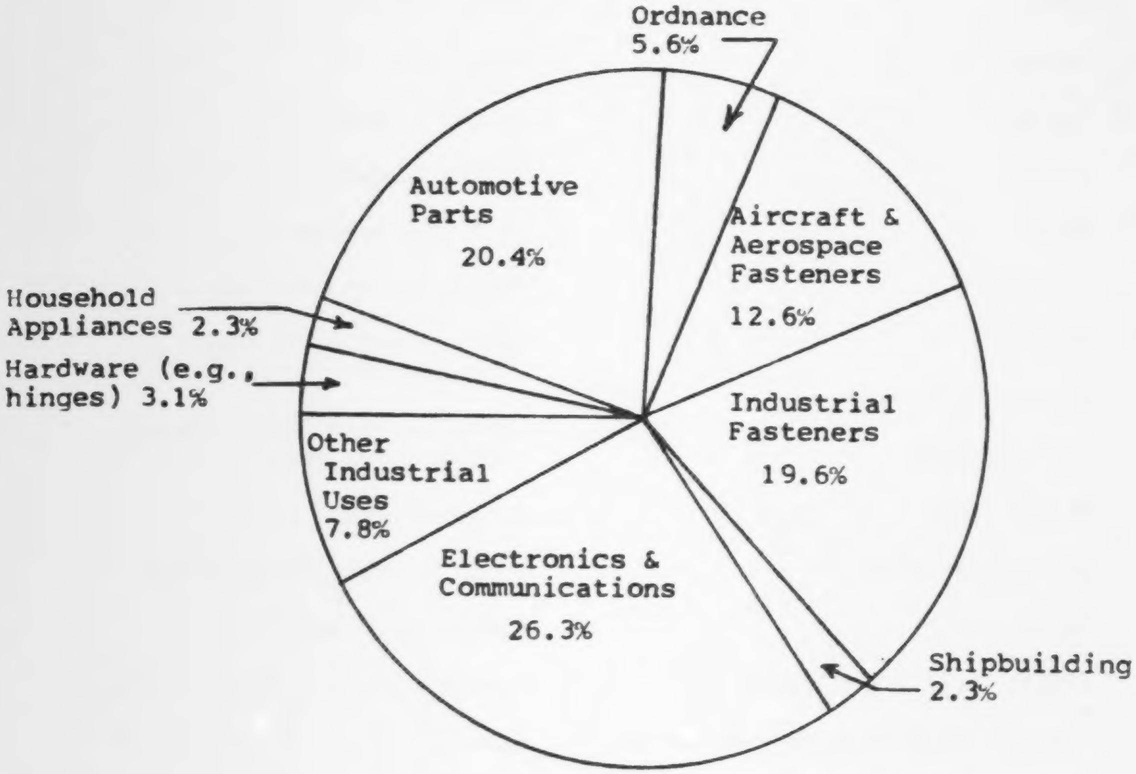
That was the position in 1974, and it can be seen that electroplating is an important application for cadmium. This is a rapidly changing world, but we must do what we can to ensure that any changes are made for the better. Changes hastily made and for the wrong reasons can have disastrous consequences. This workshop is entitled "Alternatives to Cadmium Plating." The purpose of this paper is to point out some of the unique characteristics of cadmium plating and to demonstrate that cadmium plating should retain an important place as a unique cost effective protective coating for metals.

Preservation of the environment is a matter of the greatest concern to us all. The metals-producing and electroplating industries have demonstrated their ability to meet the increasingly stringent environmental controls now being imposed. The cadmium plating industry is no exception. The industry is meeting its obligations as regards effluent control and the cadmium plating process is compatible with high standards for the environment. We can therefore confine ourselves to making a cost-benefit analysis to determine what may be the result of using a particular alternative to cadmium plating. Some of the benefits of using cadmium are not immediately obvious, and ill-considered changes can be hazardous or costly.

What of the present uses of cadmium plating in the U.S.A.? The following pie chart shows how an average annual consumption of 5,400,000 lbs. was utilized in the U.S.A. from 1965-1974.

CADMIUM USAGE - PLATING IRON AND STEEL PRODUCTS FOR CORROSION PROTECTION

Consumption of Cadmium in Electroplating By End Use [2-11]



Average Values for Consumption from 1965-1974

of 5,400,000 pounds

Taken from Cadmium Utilization Environmental Impact Materials and Process Specifications and Substitutes by E. J. Dyckman, Naval Ship Research and Development Center, June 26, 1975

In order that you may have an appreciation of the diversity (and essentiality) of the use of cadmium plating, here is a list of components which are typically cadmium-plated.

- Fasteners
- Nuts
- Bolts
- Screws
- Washers
- Rivets
- Nails
- Fittings
- Tools
- Electrical connectors
- Rifle barrels
- Mortar Tubes
- Carburetor Parts
- Magnet parts
- Clutch throw out plungers
- Aircraft undercarriage components
- Titanium aircraft parts coated with cadmium followed by molybdenum disulphide*
- Diode holders
- Voltage regulators
- Electrical relays
- Textile machinery
- Metal cutters
- Turbine engine blades
- Vanes and cases
- Piano wire
- Catapult hooks
- Marine hardware
- Pole line hardware
- Metal cutting machinery
- Cast and Malleable iron components
- Low alloy steel heat treated below 200 K psi
- Actuator arms
- Be-Cu bushings and bearings
- Compressor blades
- Dissimilar metal faying surfaces
- Gears
- Shafts
- Splines
- Shrouds
- Stainless steel bushings
- Tools

---

* Where the aircraft will meet extreme temperature conditions.

Following are some of the U.S. specifications and standards calling for the use of cadmium.

MATERIALS AND PROCESSES SPECIFICATIONS AND STANDARDS CALLING FOR THE USE OF CADMIUM

Military Specifications

MIL-STD-171
MIL-STD-454C
MIL-STD-870
MIL-STD-889A
MIL-STD-1500 (CdTi)
MIS-S- 5002C
MIL-P- 23408A
QQ-P- 416C
MIL-C- 8837
MIL-C- 81562
MIL-C- 0026482F (Navy)
MIL-C- 005015F (Navy) Contact plating
MS Sheet Forms including:

Nuts	MS-9882, 9881, 51968C, 51967D, 27040B
Bolts	MS-9088-91, 9146-51, 9441-48, 9451-57, 9458A, 9459A, 9942, 9926, 9941, 9927, 9928, 9946, 9929, 9947, 9944, 9932, 9937, 9933-36, 9914-18, 9688, 9689, 9691, 9693, 9924, 9518-26, 9530-37, 9217, 9222, 9681, 9938, 9920, 9919, 9208-14, 9219, 9221, 9223, 9680, 9682, 9683, 9218, 35754B, 9400-02, 9397-99
Washers	MS-27183D
Screws	90728C, 90727D, 51095E, 18153C, 18154C, 51106C, 90725C, 90726B, 35458B, 35457B, 16998D, 16997C, 24667A, 24677A, 24678B, 21318A, 9449, 9940, 9939, 9930, 9931, 9913, 9921 9527, 9516, 9517, 9216, 35206F, 35207F, 9215, 9206, 9207, 9528, 35190D, 35223B, 9184, 9183A, 51975A, 24629C.

Industrial Specifications

ASTM-A-165
AMS-2400M
AMS-2401
AMS-2416
AMS-2419
AMS-2426

Let us now consider the special qualities of cadmium plating which led to its use for these components and very widespread presence in military and aircraft industry specifications.

Plateability

Cadmium plating requires only very simple control of plating solutions. It is less demanding as regards surface preparation as compared to zinc. Cast and malleable iron components are easily plated with cadmium in barrel plating, because cadmium electroplate offers unusual ability to bridge pores in the basis metal, cadmium's hydrogen overvoltage favors the deposition of cadmium rather than hydrogen.

Corrosion Resistance

More resistant to some corrosive environments than zinc, cadmium's corrosion products are always less voluminous, reducing the possibility of cracking bolted joints or binding sliding surfaces. It shows greater resistance to wet storage stain.

In bimetallic couples, the following table allows comparison of cadmium's role(2). Metals with a relatively large difference in electrode potential can be effectively separated by cadmium. The electrode potential of cadmium in sea water is 0.43V; lying between aluminum, 0.52V; and mild steel, 0.34V. That of zinc is 0.76 volts.

Cadmium and zinc are the only two plating materials which can provide the benefit of galvanic protection for steel. The position of cadmium in the electromotive series means that it is able to provide galvanic protection to steel but since the difference in potential is relatively small there is no tendency for cadmium to "overwork." Thus, while it will not cover a large expanse of bare steel with its protection, it will provide long term protection, and without undue production of corrosion products. Tin plated steel, when exposed to the atmosphere, will rust overnight because tin is cathodic to steel and will induce severe corrosion because a large area of tin (cathodic) is related to a small area of steel. Plating with cadmium before application of tin will prevent this problem and provide a corrosion resistant bright finish.

Cadmium plating of copper alloys, stainless steel and aluminum provides a long lasting finish because the galvanic couple does not stimulate aggressive action from the cadmium.

In general, cadmium is the preferred galvanically active coating for use in "factory" atmospheres.

Effects of metallic contacts on atmospheric corrosion

		Affected metal										
Number	Investigated metal	1	2	3	4	5	6	7	8	9	10	11
1	Carbon steel, cast iron	-	B	B	B	B	B	A	A	A	B	B
2	Stainless steel	A	-	A	A	A	A	A	A	A	A	A-B
3	Nickel and nickel alloys	A	A	-	A	B	A	A	A	A	A	A-B
4	Chromium	A	A	A	-	A	A	A	A	A	A	A
5	Copper and copper alloys	A	B	B	B	-	A	A	A	A	A	B
6	Aluminum and aluminum alloys	B	B	B	B	C	-	A	A	B	A	C
7	Zinc and zinc alloys	C	C	B	B	C	B	-	B	B	B	C
8	Cadmium	B	B	B	B	B	B	A	-	A	A	B
9	Magnesium and magnesium alloys	C	C	C	C	C	B	B	B	-	C	C
10	Lead, tin and their alloys	A	B	A	B	B	A	A	A	A	-	B
11	Silver, gold, platinum (rhodium, palladium, osmium, iridium)	A	A	A	A	A	A	A	A	A	A	-

Columns 1 to 11 correspond to the description on the row with the same number.

A: There is no effect of contact of the metals on the corrosion of the investigated metal.

B: There is a small effect of contact of the metals on corrosion of the investigated metal, but is is significant only in very aggressive atmospheres.

C: Strong effects in outdoor exposures, and also exceptionally, in aggressive indoor climates.

One alternative to cadmium plating is zinc plating. V. E. Carter of the British Non-Ferrous Metals Research Association (now BNF Metals Technology Centre) has compared the corrosion resistance of the two(3). Greater coating thickness of zinc can be used on account of its lower cost but cadmium performs better in contact with aluminum and in enclosed spaces in high humidity(4, 5, 6, 7), especially at elevated temperatures (tropical conditions). Where coating thickness must be kept to a minimum, say 5 μm, cadmium performs better than zinc under marine and alkaline conditions(8). It is 2 or 3 times more resistant to organic vapors from electrical insulation(9) and is more resistant to the formic acid from paint films.

In the textile industry, zinc corrosion products can cause deterioration of some fabrics whereas cadmium has no adverse effect. In the weaving industry in the U.K. cadmium plating is regarded as essential for protection of fasteners and pins in water jet looms. High humidity in the conventional shuttle loom weaving shed can lead to corrosion which can jam machinery solid over a weekend. Cadmium plating provides better protection and a necessary supplement to the lubrication used. Parts which are to be disassembled after service in a corrosive environment should preferably be plated with cadmium. Bolted connections will not seize and electrical conductivity will be maintained.

When codeposited with nickel, a corrosion resistant coating of unusual quality is created(10). P. S. Willcox of ITT has commented that the intermetallic compound formed between nickel and cadmium seems quite unique as it has a high melting point and is quite low on the electromotive series. Ni-Cd diffused coatings are used for compressor parts in low alloy steel (max. U.T.S. 140 Kg/mm), 12-14% Cr, 18-8 Cr Ni steels and nickel based alloys. These materials are less susceptible to hydrogen embrittlement and permit the use of dense cadmium deposits(11).

Low-alloy steel parts which operate in jet engines at temperatures up to 1000°F have been protected from corrosion with 0.0003 in. (7.6 μm) of nickel plus 0.0001 in. (2.5 μm) of cadmium diffused at 630°F (332°C)(12) for one hour. This coating could withstand 100 hours salt spray without rusting even after 23 hours at 700°F (372°C) and one hour at 1000°F (539°C) prior to exposure.

Three independent studies have shown that chromate-treated cadmium over nickel offers the best conductive corrosion-resistant finish for aluminum.

Recent work by McDonnell-Douglas has shown that for aluminum a diffused cadmium over nickel coating, proprietary to Stanford Applied Engineering(13), meets conductivity requirements and successfully passed 816 hours of salt spray exposure (salt spray tests to ASTM B117-73). This may be a development of the R.W. Moeller technique(12, 14).

Jankowsky(15) found cadmium with chromate conversion coating over nickel to be a superior coating for aluminum (6061 T6 panels) and advocated its use. His testing involved 25 cycles, each cycle consisting of 16 hours at 200°C (392°F) followed by 32 hours of salt spray exposure. That is 800 hrs. salt spray plus 400 hrs. elevated temperature exposure.

Willcox has shown that cadmium, with chromate conversion coating, over nickel on a variety of aluminum alloys, 2024, 2011, 7075, die cast A380, and 6061, has successfully withstood 500 hours of salt spray exposure(16).

Torque Resistance

Cadmium-plated components have an inherent lubricity and demonstrate lower torque resistance than zinc plated components(17, 18) and exhibit a more constant torque resistance than is the case with lubricants. In some cases, this will be a vital consideration. A cadmium plated part will not gall when in sliding contact. On this account, if an assembly is to be subject to corrosion and then dismantled for maintenance, it is necessary that cadmium plating be used.

Formability

More ductile than zinc, cadmium plate allows easy forming after plating.

Electrical Resistance

Cadmium has a relatively low electrical resistance(7) even when provided with a chromate conversion coating for additional corrosion protection.

Jamming

Cadmium corrosion products are closely adherent and not voluminous. This reduces the danger of fouling switches and relays and makes cadmium plating ideal for the return springs in automobile brakes and clutches and for hydraulic rams used in the coal industry.

Solderability

Cadmium surfaces are excellent for soft soldering(7, 8, 17).

Appearance

Cadmium retains brightness for excellent decorative appeal.

Hydrogen Embrittlement

After cadmium plating from cyanide solutions, high strength steel, such as is used for aircraft landing gear, can be baked to eliminate hydrogen embrittlement. In general, hydrogen can be baked out through an initial flash of cadmium of thickness about 2.5 microns (.00005 mils). Because cadmium can be plated at approaching 100% efficiency, subsequent cadmium plating can be carried out over this initial flash without danger of hydrogen embrittlement(19).

High Temperature Operation

Cadmium plated steel parts can operate under stress at temperatures up to 900°F (482°C) provided that a nickel undercoat is applied before cadmium plating followed by a diffusion baking operation.

Compatibility with Adhesives

Cadmium provides an excellent bond when adhesives are used, this is true even for passivated coatings. Problems may occur when passivated zinc coatings are used and expensive adhesives may become obligatory. A decal placed over cadmium plating will not be displaced by any corrosion products.

Conclusions

When considering whether an alternative for cadmium plating can be justified, it is not only necessary to consider carefully what cost penalty may be incurred, but to pay particular attention to some of the above vital and beneficial characteristics which are not always apparent at first sight.

Cadmium electroplaters can comply with needed pollution control regulations. We, therefore, question the need to develop "Alternatives to Cadmium Electroplating in Metal Finishing."

Cadmium electroplating need not be a threat to the environment and we must be sure that we do not risk failure of life supporting components because we have not given careful thought to the implications of finding alternatives to cadmium plating.

REFERENCES

1. "Cadmium - The Metal of Benign Neglect", R. L. Stubbs, Cadmium Association London.

2. Table 13 "Protection Against Atmospheric Corrosion" by Karel Barton, translated by John R. Duncan, John Wiley & Sons, New York.

3. "The Choice Between Cadmium and Zinc Plating for the Protection of Steel", by V. E. Carter, Metal Finishing Journal, October 1972, p. 304-306

4. P. T. Gilbert, BNF Metals Technology Center, Miscellaneous Publication No. 457, 1954.

5. P. T. Gilbert and S. E. Hadden, Journal of Electrodepositors Technical Society, 1950, 25, 41.

6. F. Obgurn, Product Engineering, 1949, 20 (12), p. 135

7. S. J. Beyer, Plating, 1960, 47 (12), 1361.

8. P. F. Norrish, Corrosion Prevention and Control, 1957, 4 (8), 51.

9. G. Kloetz, Galvotechnik, 1965, 56 (9), 514.

10. Kudryavtsev N.T., IX Intern Kolloquim Tech, Hochschule Illmenau, Galvanotechnik 9, 10 (1964).

11. "Diffusion Characteristics of Heat Treated Electro-Deposited Nickel Cadmium Coatings and their Effects on Micro-Structure and Hardness of Cadmium", thesis by M. P. Malik, submitted to University of London, April 1975.

12. "Diffused Nickel Cadmium as a Corrosion Preventive Plate for Jet Engine Parts" by R. W. Moeller and W. A. Snell, Plating, 42, December 1955, p. 1537.

13. "Materials and Processes Design Data", Bulletin No. 10-02, Dept. E 457, McDonnell-Douglas Astronautics, St. Louis (1975).

14. Aerospace Material Specification 2416, Society of Automotive Engineers, New Your, 1968.

15. E. J. Jankowsky, Report No. NADC-76274-30, Naval Air Development Center, Warminster, Pennsylvania, 1976.

16. P. S. Willcox, unpublished research 1976-7, ITT Cannon Electric, Santa Ana, California.

17. D. N. Layton, Trans I.M.F., 1965, 43(4), 153.

18. G. David, Corrosion (Paris) 1969, 17(7), 343.

19. Private communication with L. Morin

Unique Characteristics of Cadmium Electroplating

MR. GROBIN: Allen Grobin, IBM Corporation. I think you have adequately demonstrated the place of cadmium in the electroplating industry; however, do you think we have been using cadmium where it wasn't necessary? Could we possibly reduce the environmental hazards by using, say, zinc in many of the applications where today we specify cadmium because of the reputation that cadmium has gained, justified or not?

MR. COOK: I think that is possible; however, the considerably increased cost of plating cadmium compared with zinc, for example, should mean that those instances are really at a minimum; however, I am quite sure that those instances will occur.

MR. DROSTEN: Fred Drosten, Army Aviation Research and Development Command, St. Louis. I think you made an error on your tabulation showing Cd plating on titanium. There have been some cadmium embrittlement instances of the titanium definitely traced to cadmium plating.

MR. COOK: Thank you for pointing that out. My reference apparently was at fault. I think we should make that change in the final paper.

MR. MEYER: I am Fred Meyer, Air Force Materials Lab. There are many occasions where we find other materials have better corrosion resistance than cadmium. I think we should not rely totally on saying, "we have the good material. Let's not look for anything else."

Some of the materials we have looked at are definitely superior from the service standpoint. Tomorrow, I will be giving a paper with actual service tests. This is one thing we haven't seen quite yet. We have laboratory salt spray tests which have a certain degree of value, but the final criteria are how well does it perform a service?

In certain aircraft applications, we are advocating the use of other coatings because they are superior from the corrosion standpoint.

I am also wondering whether, ultimately, a good bit of the cadmium plating usage may be picked up in the rapidly developing battery areas. There is probably a good chance they will be using more cadmium in batteries in the future.

This meeting has been set up for the purpose of determining available alternatives. We shouldn't totally abandon cadmium because it is an environmental hazard, but probably the number of applications will diminish because we do have alternatives.

MR. COOK: I think that the cadmium plating industry would be very happy to bow out of any application where a cost-benefit analysis has demonstrated some improved coating is available.

I think we have to be careful of relying upon accelerated tests. There is no accelerated test which will adequately demonstrate what will happen in service. I say that unequivocably.

You are faced with long-term testing of these materials. The hygiene point of view is again being brought up. I think it should not be brought up because our premise is that the cadmium plating industry can operate within whatever controls may be set up. It is up to the regulatory agencies to set up those controls, and let us operate within those limits. Then let the economics decide where we go from there.

MR. HEIDERSBACH: BoB Heidersbach from Ocean Technology Incorporated. The one thing absent from your presentation, is the fact that while cadmium has its problems during the plating process as far as the elimination of hydrogen in the substrate metal is concerned, once the cadmium has been applied after a proper bake-out procedure, it is a very effective barrier to the further introduction of hydrogen into the substrate.

This is at least one application where I am unaware of another coating material that is as effective in a hydrogen or hydrogen sulfide or hydrogen cyanide environment.

MR. COOK: Thank you very much. I should have made that stronger. A zinc coating is impervious to hydrogen and will prevent hydrogen from getting in and getting out.

MR. DROSTEN: Fred Drosten, Army Aviation Research and Development Command. How is it you quote salt spray tests, accelerated tests, and yet say they are not valid? I am looking for experience like Mr. Meyer can supply.

MR. COOK: I think that is a point well taken. I think salt spray tests are very useful in the laboratory for putting materials into some descending order of corrosion resistance, if you like, with a tongue in cheek, because in actual service, that order is going to be disturbed anyway, and you haven't got anything else.

The fact that you haven't got anything else shouldn't lead you to risk using some other coating on a life-supporting component. You shouldn't just say, "In salt spray tests it was perfectly all right, and it is just too bad that in practice it didn't do too well."

I think we heard that in previous papers.

MR. MUEHLBERGER: Don Muehlberger, McDonnell Douglas. From an environmental standpoint, isn't part of the problem not only how to clean up the plating baths during the plating process, but what to do with the cadmium that you have in fact cleaned up and now have some place within the plating area? Also, what happens to the cadmium on the plated part that now enters the environment?

MR. COOK: Yes. I think regarding the cadmium in sludge, for example, it is the responsibility of the cadmium industry to work out recycling techniques.

We mentioned other applications for cadmium. I think that the nickel-cadmium battery for a hybrid vehicle is a wonderful application which ought to be further pursued.

Cadmium is used in the lead acid battery grid, for example, and at one and a half percent in some grids. Gould Corporation, for example, uses it, so there are other applications.

Regarding the use of cadmium electroplate and its effect on the environment, so far as I know, the tests have not shown any problem.

Dr. Yost would be more qualified to talk in the environmental field then I am.

MR. GROBIN: I am Allen Grobin, IBM Corporation, and a member of ASTM Committee B-8, which is now the jurisdiction of Committee G-1. The salt spray test while initially developed as a corrosion test was very quickly found not to be a corrosion test. Many of the metal plating specifications disqualified the salt spray test as a corrosion test. It is a comparative test for quality control and should not be used as an evaluator of corrosion resistance. It should not be used to compare the resistance of one type of plating against another.

All you can do is compare a single plating against itself. That is, are you producing it today the way you produced it yesterday?

Alternative Materials and Processes

Session III

Wednesday Morning 10:40

THE PROPERTIES OF CADMIUM AND TIN-ZINC ELECTRODEPOSITS

John M. Bihl
Tin Research Institute, Inc.
Columbus, Ohio 43201

Laboratory tests have established that tin-zinc alloys of suitable composition, 75-80% tin, provides corrosion resistant properties equivalent to or better than cadmium in certain environments. Tin and zinc, are widely used as coatings for protection of steel against corrosion. Tin itself is resistant to atmospheric corrosion, but since tin is cathodic to steel, rust develops at pore sites. Zinc is anodic to steel and protects the base metal through sacrifical action. However, an electrodeposited composit of tin and zinc results in a compromise of reducing the porosity of the coating and the rate of sacrifical attack of the zinc.

A comparison of the corrosion properties of tin-zinc alloy with cadmium on steel shows the alloy to have slightly inferior corrosion properties in marine atmospheres but superior to cadmium in industrial atmospheres. For long term protection of steel coated with tin-zinc or cadmium in contact with aluminum alloys, the tin-zinc proves to be the favored coating in both industrial and marine environments.

As plated tin-zinc has a mat silver-white finish that can be polished to a high luster, good anti-friction properties and solderability superior to that of cadmium. The deposit is usually plated from an alkaline potassium stannate zinc cyanide electrolyte, although non-cyanide electrolytes have been shown to be practical. The stannate zinc cyanide electrolyte provides excellent throwing power, far superior to the typical cadmium cyanide electrolyte.

Preceding page blank

THE PROPERTIES OF CADMIUM AND TIN-ZINC ELECTRODEPOSITS

John M. Bihl
Tin Research Institute, Inc.
483 West Sixth Avenue
Columbus, OH 43201

A number of electrodeposited metallic coatings are used for protection of steel, aluminum and other metals against various corrosive conditions. Tin, zinc and cadmium deposits are commonly used for this purpose, each having its advantages as well as limitations. A satisfactory electrodeposit used solely to prevent the corrosion of steel, for example, should furnish sacrificial (anodic) protection of the steel base. Zinc and cadmium are two protective metals capable of being easily deposited from an aqueous electrolyte that furnish this anodic protection to steel. But, while providing good sacrificial protection, zinc is itself consumed in the process which usually results in a white corrosion product that not only deteriorates the aesthetics of the plated parts, but renders them unsolderable and in certain cases can cause interference with the electrical or mechanical operation of the plated items. In the case of cadmium, it is well known that this metal affords good sacrificial protection to steel in humid and marine atmospheres, but its protective value in an industrial atmosphere is limited. In contrast to zinc and cadmium, tin itself is resistant to atmospheric corrosion, but under most conditions tin is cathodic to steel which results in the rusting of the steel at pore sites.

As an alternate to cadmium, zinc or tin, a tin-zinc alloy coating of suitable composition, usually 70-80% tin, provides excellent corrosion protection with fewer limitations in many applications than these pure metals. Thetin-zinc alloy as-plated has a fine-grain crystalline structure, a silvery-white color and a mat finish which can be polished to a high luster (Fig. 1). The solderability of the 75-25 tin-zinc alloy is superior to cadmium or zinc, but inferior to tin or a 50-50 tin-lead coating, in solderability tests indicating area of spread (Fig. 2). The plated alloy is ductile permitting forming and deep drawing.

The 75-25 tin-zinc alloy provides a coating which is slightly anodic to steel, a property that gives sacrificial protection to the steel at pore sites or discontinuities in the coating, but at a sacrificial rate that is less than that of a pure zinc deposit. Further, the unsightly white corrosion product commonly associated with zinc does not appear on the surface of the tin-zinc plated items, even after long periods of service.

Tin and zinc can be co-deposited in all proportions from an electrolyte containing sodium or potassium stannate, sodium hydroxide, zinc cyanide and free hydroxide, either sodium or potassium (Fig. 3). The use of the potassium salts leads to an improvement in the conductivity of the electrolyte which permits the use of higher current densities. Satisfactory operation of either the potassium or sodium bath requires the anodes to be operated in the filmed condition to insure the dissolution of tin in the stannate form. The composition of the deposit is changed by variations in the zinc and hydroxide content of the electrolyte while bath temperature, current density, tin content, and total cyanide do not have a significant effect on the deposited tin-zinc ratio.

Davies and Angles[2] made investigations into the deposition of tin-zinc from cyanide-free alkaline solutions containing trisodium salt N-hydroxyethylethylenediamine triacetic acid, sodium hydroxide, sodium stannate and zinc carbonate. The electrolyte was found to be stable and the deposits obtained were similar to those obtained from the conventional stannate-cyanide electrolyte. Satisfactory deposits from a fluoborate electrolyte in the 70-30 tin-zinc range have also been obtained by Cohen[3]. However, there has been no commercial use of either of these two formulations.

Alternately, tin-zinc can be deposited by a mechanical process developed by the 3M Company. In this process the powdered metals, in this case tin and zinc, are cold welded to the base material in a rotating barrel containing water, glass beads and proprietary promoter additives. The glass beads provide the peening action necessary for the cold weld process. Mechanical plating has the advantages of reduced waste disposal problems and lack of hydrogen embrittlement.

Tin-zinc plate of any composition can be passivated to enhance its protective value by treatment in a hot 2 percent chromic acid solution or a solution of sodium dichromate containing 0.33 percent by weight of sulphuric acid. From the corrosion viewpoint, it is usually not necessary to passivate tin-zinc but a chemical surface treatment will improve the corrosion resistance, serve to reduce finger marking, and provide better paint adhesion without impairing solderability significantly. Figures 4 and 5 show the improved protection provided by chromic acid treatment of a 80-20 tin-zinc plate (100μin.) on steel panels subjected to 192 hours in a humidity chamber and to salt spray.

Since tin-zinc can be plated in all proportions a program was undertaken at the Tin Research Institute to determine the most suitable tin-zinc ratio in terms of corrosion resistance. Plated steel panels of tin, zinc, cadmium and tin-zinc, ranging from a 92-8 to a 28-72 ratio, at thicknesses of 300, 500 and 700μin., were subjected to 400 hours of salt spray and to 1,100 hours of humidity testing.

The results of the salt spray (Fig. 6) show heavy rusting on the tin and cadmium samples at all thicknesses while the zinc coatings were almost entirely converted to a whitish corrosion product which then allowed massive rusting of the base steel. Tin-zinc panels of 92-8 composition exhibited localized rusting due to the limited anodic protection afforded by the zinc while the 28-72 tin-zinc panels showed excessive amounts of the white corrosion product from the zinc. The alloys of the 86-14 and 78-22 tin-zinc ratios provided adequate protection and retained good aesthetics at all thicknesses.

The relative corrosion resistance of similarly plated panels subjected to humidity testing (Fig. 7) indicated pore site rusting where tin alone was used as a protective coating. Panels of plated tin-zinc in the 70-80 percent zinc range not only provided adequate protection but again retained much of their aesthetic value. Zinc provided the needed base metal protection but the appearance of the panel deteriorated rapidly. The cadmium-plated panels performed well in the humidity tests.

Since it is important that a protective coating remain protective even after the base metal is deformed, steel test panels of plated tin, zinc, cadmium and the 78-22 tin-zinc alloy were exposed to humidity tests after being deformed by cupping (Fig. 8) and by bending and reflattening (Fig. 9). In both cases the tin and cadmium coatings were damaged and rusting of the base steel occurred. The tin-zinc like the pure-zinc-plated panels were little affected by deformation.

The protective value of a coating in an industrial environment becomes another important area for investigation. The results of 200 days outdoor light industrial exposure of steel panels plated with 500μin. cadmium and 78-22 tin-zinc provided evidence that the tin-zinc was far superior to cadmium in this case (Fig. 10).

With the increasing use of aluminum by the automotive and other industries, the need to prevent galvanic corrosion between aluminum and steel components is critical. The extensive use of steel fasteners to secure aluminum alloy structures led the Tin Research Institute to undertake a program to study methods of preventing this galvanic corrosion. Since tin-zinc has a galvanic potential near that of aluminum, it was natural to try plating the steel fasteners with tin-zinc.

To study this complex problem, steel nuts and bolts coated with cadmium, zinc and the 75-25 tin-zinc alloy were mounted in aluminum plates and subjected to suburban and marine atmospheres, laboratory salt spray and exposure to the sea at mid-tide level. Tests indicated that the corrosion protection afforded by both zinc and tin-zinc was superior to that of cadmium after exposure to 974 days in a suburban atmosphere (Fig. 11). Exposure to a marine atmosphere for 684 days showed the rather poor performance of zinc, while tin-zinc and cadmium provided adequate protection (Fig. 12). Exposure under the same conditions, marine atmosphere, for nine years, 2 months, resulted in the cadmium and zinc-plated bolts severely rusting and the surrounding aluminum experienced heavy pitting. The tin-zinc-plated bolts were still in good condition with only minor pitting of the aluminum (Fig. 13).

Laboratory tests also indicated etching of the aluminum after 326 days of salt spray in areas surrounding zinc-plated bolts. Tin-zinc and cadmium produced less severe galvanic corrosion in the salt spray tests but the aluminum in both cases did exhibit some pitting (Fig. 14).

The results obtained from exposure to the sea at middle tide level for 650 days were again somewhat different than those of other tests. Localized corrosion of the aluminum took place prior to the rusting of the coated steel components. This condition was most pronounced with the zinc-plated bolts followed by tin-zinc and cadmium. The cadmium-plated bolts and the surrounding aluminum remained in relatively good condition throughout the test (Fig. 15).

Although no protective coating is suitable for all applications, the properties of tin-zinc as a substitute coating for cadmium can find numerous applications. With its ease of plating, good solderability, excellent corrosion protection for steel in most environments and as a viable coating to prevent galvanic corrosion between aluminum and steel, tin-zinc coatings have a place in industrial as well as consumer applications.

References

1. Tin Research Institute, Publication No. 202, (1963)

2. Davies, A. E., and Angles, R. M., The Electrodeposition of Tin-Zinc Alloys from Stannate-Complexone Solutions, Trans. Inst. Met. Finishing, 33, (1956)

3. Cohen, B., Plating, Sept. 1957, 963-8

4. Hedges, E. S., (editor), Tin and Its Alloys, Edward Arnold, Ltd., London, 1960, 131

5. Tin-Zinc Coatings, Tin and Its Uses, No. 17, 5-8

6. Britton, S. C., and de Vere Stacpoole, R. W., Metallurgia, 52, 310, 64-70, (1955)

7. The Trend to Tin-Zinc Coatings, Tin and Its Uses, No. 59, 12-13

8. U.S. Patent No. 2,675,347

9. Britton, S. C., and Angles, R. M., Weathering Tests of Tin-Zinc Alloy Coatings on Steel, Metallurgia, 44, 264, (1951)

Figures and Illustrations

Fig. 1	Various tin-zinc-plated items
Fig. 2	Solderability tests of various coatings
Fig. 3	Composition and working conditions of tin-zinc alloy plating bath
Fig. 4	Humidity chamber test of passivated and as-plated tin-zinc
Fig. 5	Salt spray test of passivated and as-plated tin-zinc
Fig. 6	Salt spray test of tin, zinc, cadmium and various tin-zinc alloys
Fig. 7	Humidity chamber test of tin, zinc, cadmium and various tin-zinc alloys
Fig. 8	Humidity chamber test of tin, zinc, cadmium and 78/22 tin-zinc after cupping
Fig. 9	Humidity chamber test of tin, zinc, cadmium and 78/22 tin-zinc after bending and reflattening
Fig. 10	Outdoor exposure of 78/22 tin-zinc and cadmium
Fig. 11	Tin-zinc-, zinc-, and cadmium-plated bolts in aluminum plate exposed to suburban atmosphere
Fig. 12	Tin-zinc-, zinc-, and cadmium-plated bolts in aluminum plate exposed to marine atmosphere, 684 days
Fig. 13	Cadmium-, zinc-, and tin-zinc-plated bolts in aluminum plate exposed to marine atmosphere, nine years, two months
Fig. 14	Aluminum plate, corrosion products removed, after laboratory salt spray
Fig. 15	Tin-zinc-, zinc-, and cadmium-plated bolts in aluminum plate after exposure to sea at middle tide level

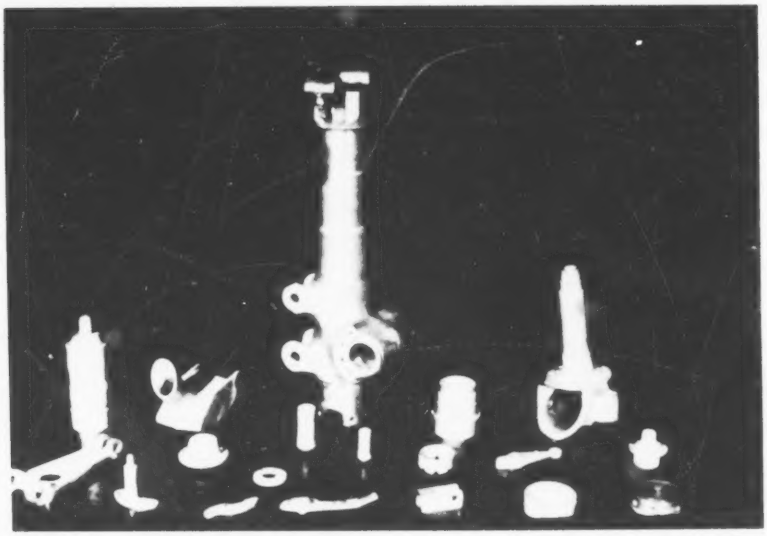
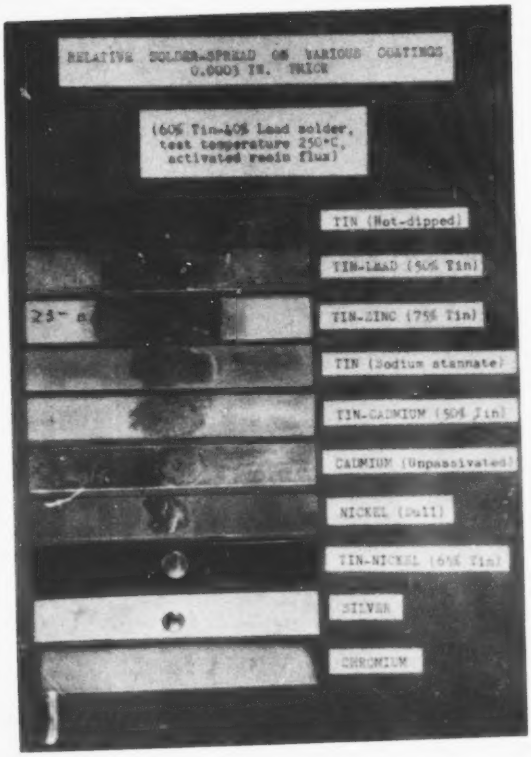
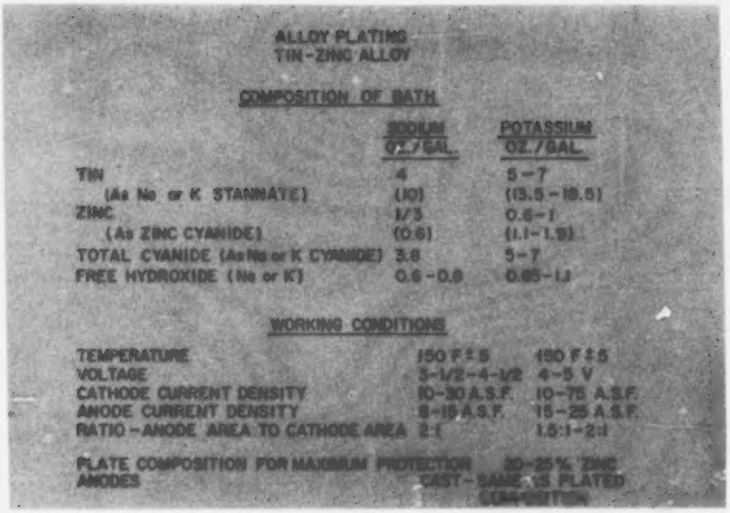


Figure 1. Various tin-zinc plated items.



Reproduced from best available copy.

Figure 2. Solderability tests of various coatings.



ALLOY PLATING
TIN-ZINC ALLOY

COMPOSITION OF BATH

	SODIUM OZ./GAL.	POTASSIUM OZ./GAL.
TIN	4	5 – 7
(As Na or K STANNATE)	(10)	(13.5 – 18.5)
ZINC	1/3	0.6 – 1
(As ZINC CYANIDE)	(0.6)	(1.1 – 1.9)
TOTAL CYANIDE (As Na or K CYANIDE)	3.8	5 – 7
FREE HYDROXIDE (Na or K)	0.6 – 0.8	0.85 – 1.1

WORKING CONDITIONS

TEMPERATURE	150 F ± 5	150 F ± 5
VOLTAGE	3-1/2 – 4-1/2	4 – 5 V
CATHODE CURRENT DENSITY	10 – 30 A.S.F.	10 – 75 A.S.F.
ANODE CURRENT DENSITY	8 – 15 A.S.F.	15 – 25 A.S.F.
RATIO – ANODE AREA TO CATHODE AREA	2:1	1.5:1 – 2:1

PLATE COMPOSITION FOR MAXIMUM PROTECTION 20 – 25% ZINC
ANODES CAST – SAME AS PLATED COMPOSITION

Figure 3. Composition and working conditions of tin-zinc alloy plating bath.

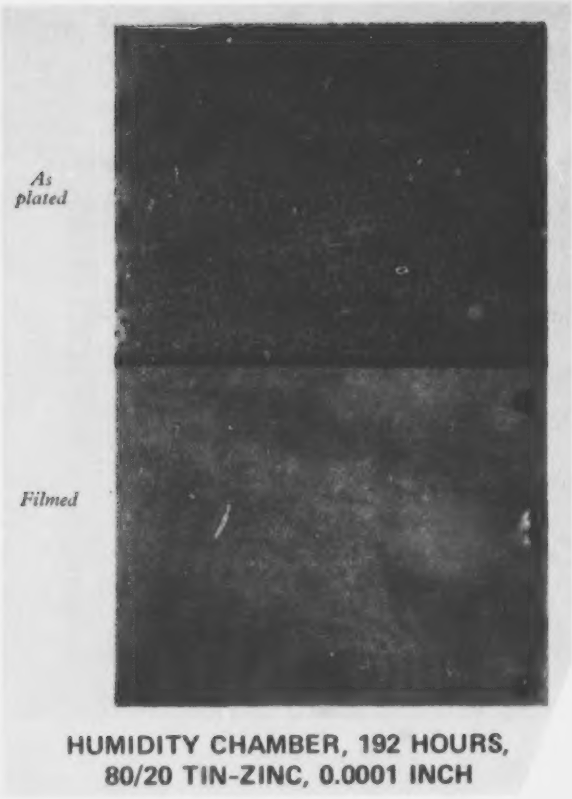


Figure 4. Humidity chamber test of passivated and as-plated tin-zinc.

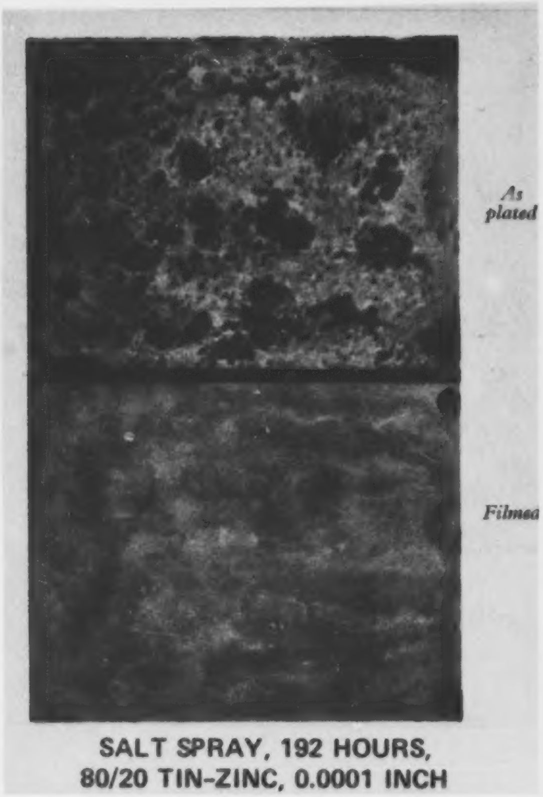


Figure 5. Salt spray test of passivated and as-plated tin-zinc.

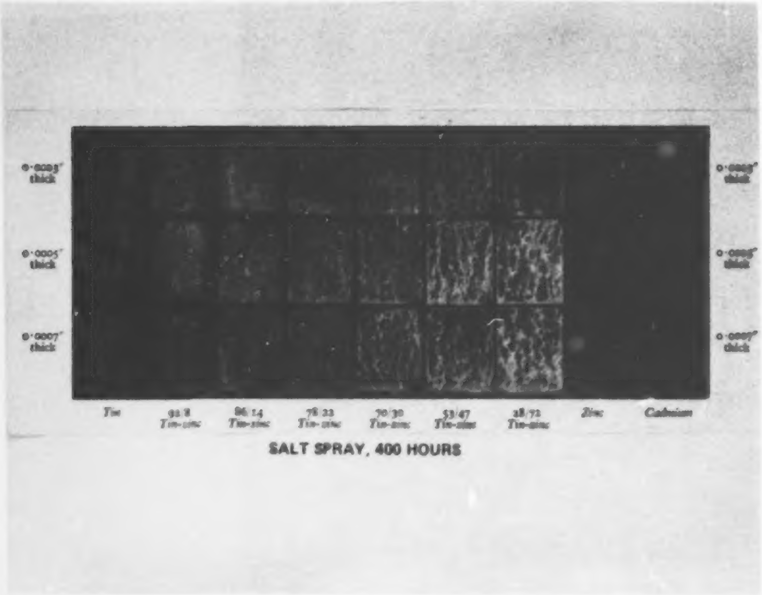


Figure 6. Salt spray test of tin, zinc, cadmium, and various tin-zinc alloys.

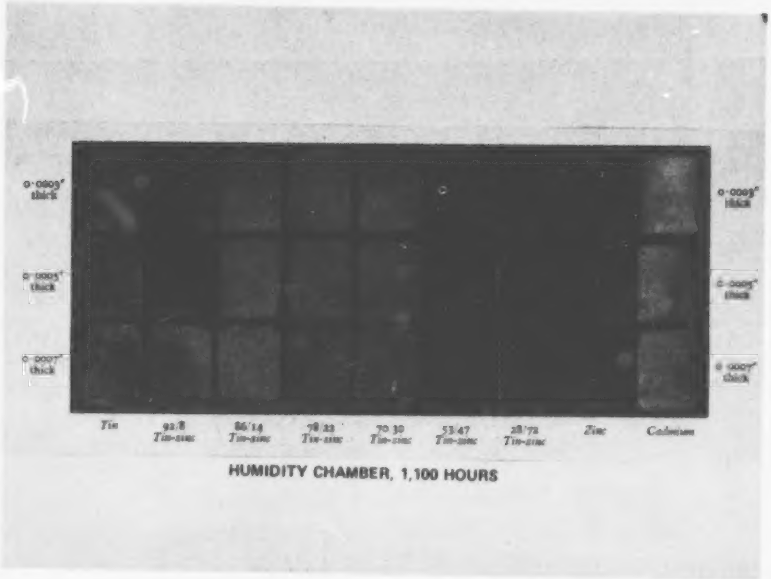


Figure 7. Humidity chamber test of tin, zinc, cadmium, and various tin-zinc alloys.

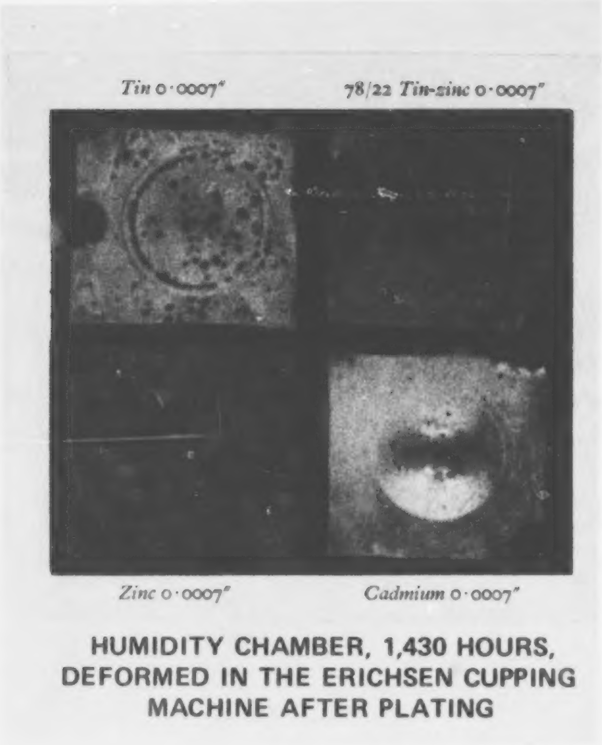
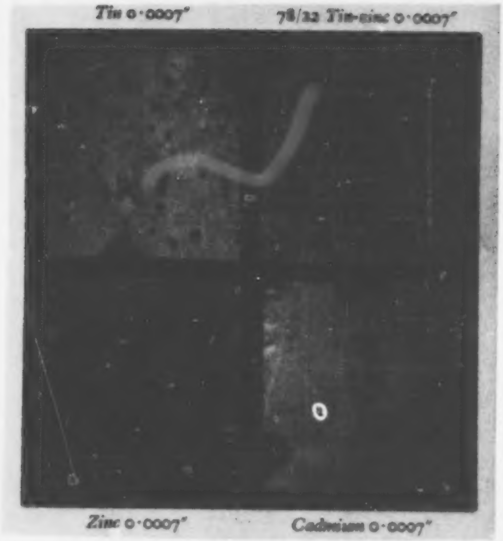

Tin 0·0007"
78/22 Tin-zinc 0·0007"
Zinc 0·0007"
Cadmium 0·0007"
HUMIDITY CHAMBER, 1,430 HOURS, DEFORMED IN THE ERICHSEN CUPPING MACHINE AFTER PLATING

Figure 8. Humidity chamber test of tin, zinc, cadmium, and 78/22 tin-zinc after cupping.



HUMIDITY CHAMBER, 1,430 HOURS, DEFORMED BY BENDING AND REFLATTENING AFTER PLATING

Figure 9. Humidity chamber test of tin, zinc, cadmium and 78/22 tin-zinc after bending and reflattening.

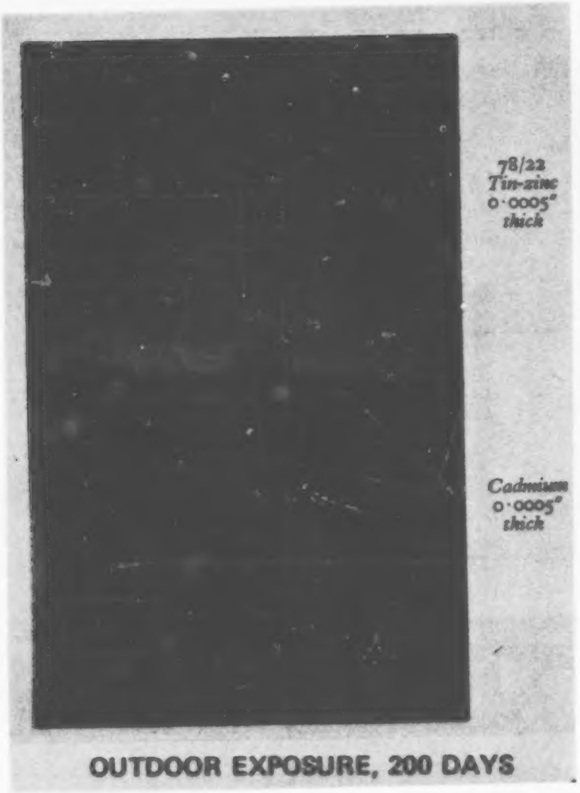
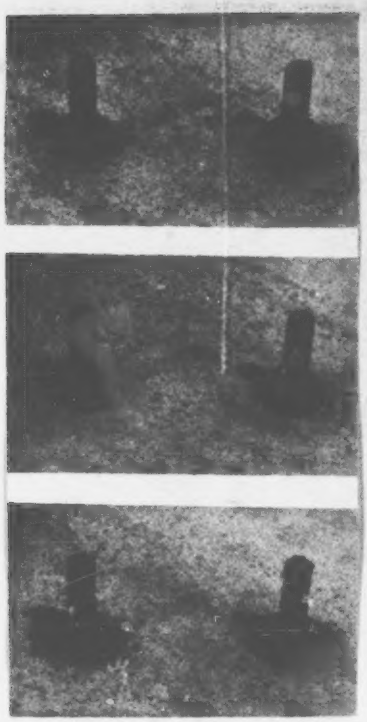


Figure 10. Outdoor exposure of 78/22 tin-zinc and cadmium.



SUBURBAN ATMOSPHERE, 974 DAYS,
UPPER TIN-ZINC, MIDDLE ZINC,
LOWER CADMIUM

Figure 11. Tin-zinc, zinc, and cadmium plated bolts in aluminum plate exposed to suburban atmosphere.

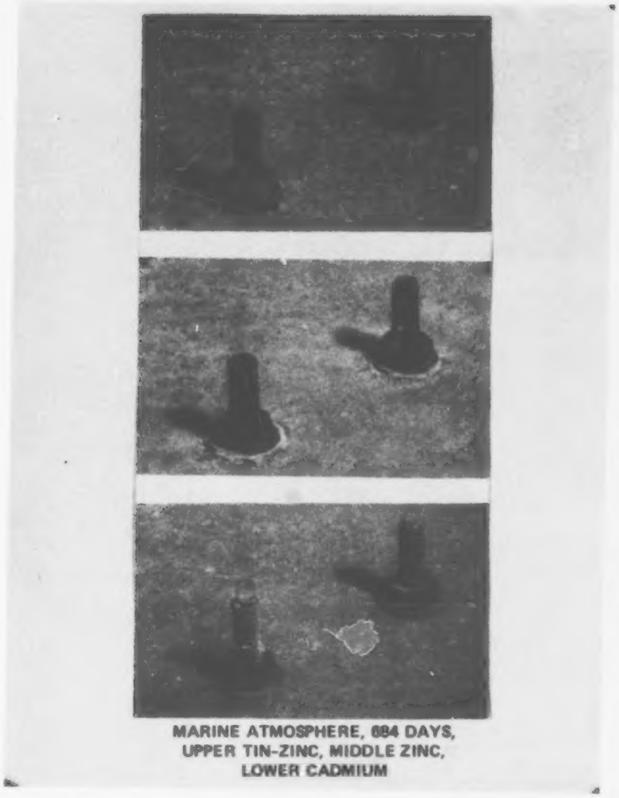


Figure 12. Tin-zinc, zinc, and cadmium plated bolts in aluminum plate exposed to marine atmosphere, 684 days.

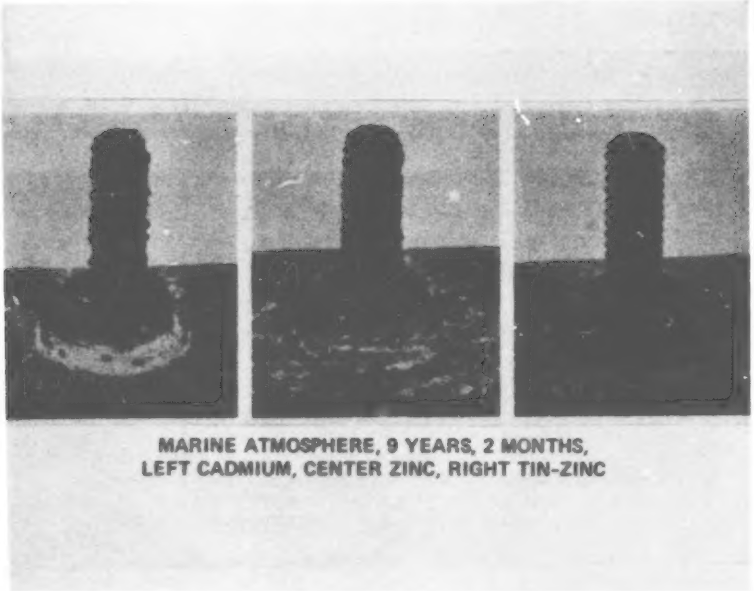

MARINE ATMOSPHERE, 9 YEARS, 2 MONTHS,
LEFT CADMIUM, CENTER ZINC, RIGHT TIN-ZINC

Figure 13. Cadmium, zinc, and tin-zinc plated bolts in aluminum plate exposed to marine atmosphere, nine years and two months.

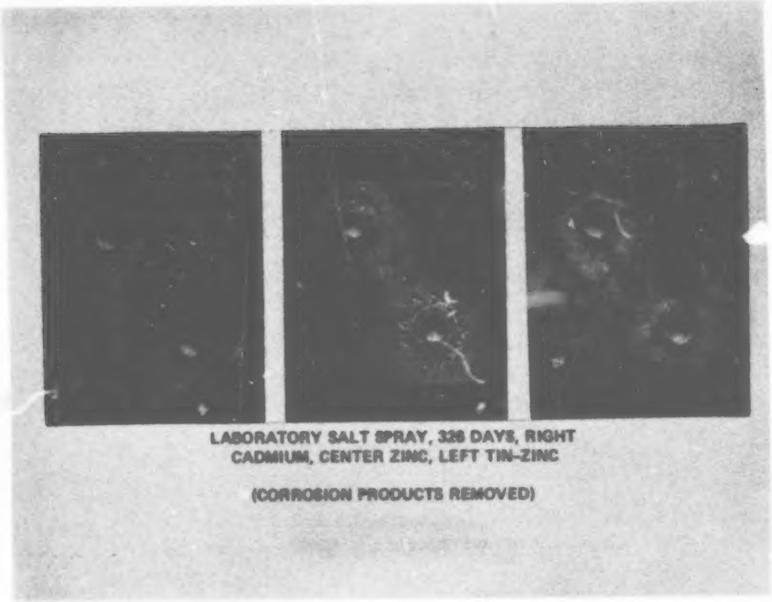

LABORATORY SALT SPRAY, 326 DAYS, RIGHT
CADMIUM, CENTER ZINC, LEFT TIN-ZINC
(CORROSION PRODUCTS REMOVED)

Figure 14. Aluminum plate, corrosion products removed, after laboratory salt spray.

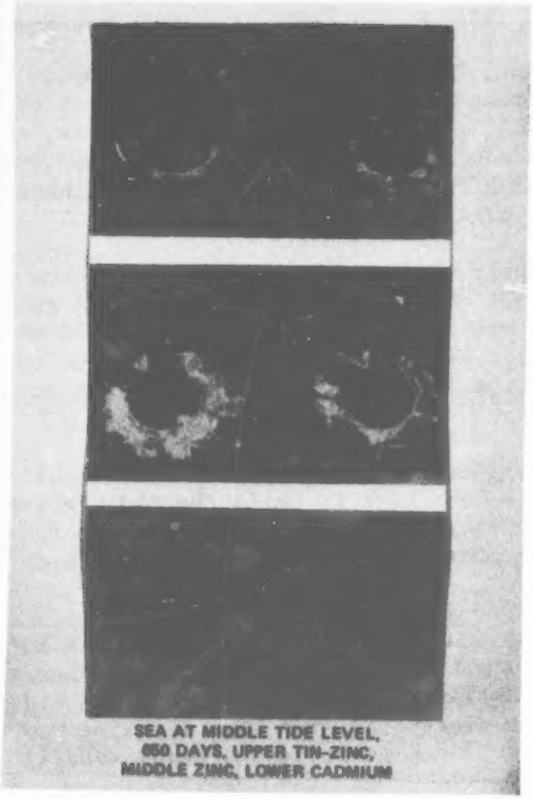

SEA AT MIDDLE TIDE LEVEL,
650 DAYS, UPPER TIN-ZINC,
MIDDLE ZINC, LOWER CADMIUM

Figure 15. Tin-zinc, zinc, and cadmium plated bolts in aluminum plate after exposure to sea at middle tide level.

The Properties of Cadmium and Tin-Zinc Electrodeposits

MR. KOVELAN: John Kovelan, Diamond Shamrock. Yesterday in my talk I made reference to Zincrometal, which is our proprietary coating which is pre-coated sheet steel, formable, weldable, paintable, non-corrosive and of course non-polluting, and it is used on 8,000,000 automobiles. I am just wondering in your objective reporting here why you didn't include any panels of Zincrometal.

MR. BIHL: One of the panels that I did show was nine years and two months old. Tin-zinc is not new. It is an alloy that is quite old. As a matter of fact, it was developed in the early '50's when there was a shortage or restriction on the use of cadmium, and it was specifically developed by the Tin Research Institute as a substitute for cadmium.

Of course, when there was plenty of cadmium metal, again with no restrictions on its use, people went back to using the old stand-by, cadmium. Only recently have we felt that there was some need to reintroduce our original work on tin-zinc and the corrosion data on tin-zinc as a possible substitute.

MR. GROBIN: Allen Grobin, IBM Corporation. I would like to point out that a number of years ago, with the Bureau of Standards Research Associate Program, Dr. Sidney Phillips of the IBM Corporation did a study of a number of alloys for electrical contact. Tin-zinc was one of these, and tin-zinc did very well for electrical contact material.

MR. TAYLOR: Ed Taylor, Standard Pressed Steel Company. I have been involved in conducting a number of global exposure programs for fasteners of many different alloys. We have coated a number of these alloys with cadmium and other metals. We have exposed these all over the world on the roofs of our various plants, on 98 cars in various countries throughout Europe, the United States, and Puerto Rico. I have never seen cadmium decompose as rapidly as you have shown, and I wonder whether this is due to the job shop or the facility where your fasteners were plated.

I am offering the facilities of Standard Pressed Steel Company for any further investigations you might have. I am sure we can do a good job and show you that Cd can be longer lasting than what you have shown.

MR. BIHL: Which particular test?

MR. TAYLOR: In general I noticed that some of your atmospheric results were very short.

MR. BIHL: We have found that cadmium is not really the best coating in an industrial atmosphere.

MR. TAYLOR: Various references attribute this to the presence of sulfur dioxide. Zinc is supposed to be much more resistant. I feel that with all the salt currently in the atmosphere as an industrial pollutant, times have changed, and perhaps cadmium is a lot better than it used to be.

MR. BIHL: This may very well be true. I will get back to my statement. These tests were run a number of years ago, and it could be that the industrial pollutants today are much different than what they were 15 years ago.

MR. TAYLOR: I just want to reiterate that we have seen cadmium plating from a number of different job shops and different companies, and cadmium plating done on different days or by different people gives completely different results.

MR. BIHL: I am sure if we continue with this study, we will take you up on your offer.

MR. MAYER: Jim Mayer, 3M Company. I wonder what the thickness was on the nut and bolt specimens you were showing.

MR. BIHL: All of them, including the cadmium, the tin-zinc, and the aluminum were plated seven-tenths of a mil.

MR. MEYER: Fred Meyer, Air Force Materials Lab. Ed was talking about atmospheric changes. Since we started removing particulate matter, the atmosphere is much more acidic. In some of the European countries, the rain has a pH of somewhere around three or four, due mainly to the removal of the particulate matter from power plant exhausts which would generally tend to neutralize the gases. The gases coming off from power plants were relatively innocuous, but now they are definitely acidic.

Like silver, cadmium is particularly susceptible to sulfur, sulfur dioxide and hydrogen sulfide. In marine environments, cadmium performs well in seawater, but doesn't perform quite as well on a carrier aircraft as it would on an aircraft flown out of a coastal area because, on our carriers, we have sulphur dioxide coming out of the stacks.

One of the big enemies of cadmium is sulphur in the atmosphere, and we are probably getting more of this in the air now than we used to. It is definitely more in the acidic end than on the alkaline end.

MR. BIHL: Yes, as a matter of fact we have done work with tin-Cd. Tin-Cd in most instances was similar to the tin-zinc. In marine atmosphere it tended to do quite well. Solderability was superior to pure cadmium. Obviously it would have excellent lubricity because of the cadmium and tin present.

MR. MEYER: Was cadmium in short supply at the time of this work?

MR. BIHL: No, some of the work was done later. I suspect that what you are asking is why I didn't present the tin-cadmium information also. Obviously, the reason I didn't is because the title of this seminar is "Alternatives to Cadmium," and I think we have an alternative to cadmium, tin-zinc, without adding cadmium back into it.

MR. MEYER: I don't think we are going to find one material that can replace cadmium across the board. I think you made the statement that there really isn't a valid total alternative, and we have to look at each application individually.

MR. BIHL: If you give me time enough to present three or four more papers, I can probably give you other tin alloys that work quite well.

MR. MEYER: Each one of these materials has its drawbacks, including cadmium. Maybe the title of the conference should have been "Substitutes," rather than "Alternatives," because we aren't going to completely abandon it.

Another topic not addressed by this conference is the various sources of cadmium wastes. If we wash airplanes and vehicles at air and naval bases and the waste water carries the metallic oxides into waste treatment plants, and if we continue to use cadmium for these applications, are we really separating it out of the end use environment, even though we are controlling the plating effluent.

What was the cost of the tin-zinc compared to cadmium?

MR. BIHL: The metal cost, will be higher. For the total overall process, I really cannot answer. We have not made a study of the treating of the cadmium waste versus the waste that would come from the tin-zinc plating bath. This is somewhat out of the realm of the Tin Research Institute. The pollution control costs for the cadmium would probably equalize the costs, or the two will be very close.

MR. MEYER: Will the tin-zinc contribute to hydrogen embrittlement?

MR. BIHL: It undoubtedly will get hydrogen embrittlement, but not extensively because zinc and tin aren't known for hydrogen embrittlement.

MS. ZILEK: I am Mrs. Carolyn Zilek from Ford Motor Company. In testing protocol on the thickness of the metal applied, do you think that it is important to check different mil thicknesses in relation to the coating? In your case, you represented results for one specific thickness, but how do these so-called alternatives stack up against cadmium when you evaluate them at different mil thickness?

MR. BIHL: The thicknesses are going to make a difference. One prime example of this would be the tin thickness. In every case here, tin showed rusting pore sites because it is cathodic to steel. If we were to put a one mil coating or a one and a half mil coating of tin on steel, the tin would exceed all the other coatings in the tests that I showed here simply because the steel would be entirely covered, and the tin itself is extremely resistant to corrosion.

Undoubtedly we are going to see variations like this with zinc, for instance. If we put a very thick coating of zinc on a strip of steel, it is going to give adequate corrosion protection to the steel until all the zinc is used up sacrificially. I assume that this would be true of cadmium and my tin-zinc also.

Our research programs tried to use something that was within the realm of practicality that is plated in our shops for use. Most of the tests were done at between one-half and seven-tenths of a mil which represents typical coating thicknesses. To get a true evaluation, we should test a whole gamut of thicknesses.

We have done considerably more tests than I have shown up here. I don't recall that any of them happen to be of different thicknesses. We have tested aluminum plates and various aluminum alloys. We did some scratch testing on plated steel.

MR. GROBIN: Allen Grobin, IBM Corporation. I want to make two comments, one on the degree of corrosion shown in your slide on cadmium. I have also seen that type of corrosion in heavy industrial environments here in the United States, and I think part of the problem is that cadmium plates so well that many platers do not plate it on adequately prepared substrates.

The other platings require more stringent preparation techniques to achieve fewer pores and a more adherent coating.

MR. BIHL: That is a point well taken.

MR. SIMMONS: Gene Simmons, Sermetel, Incorporated. How reliable is the quality of the tin-zinc from source to source?

MR. BIHL: In starting up any new plating line, there are going to be some problems. In general, plating tin-zinc should not be difficult. It is basically run like an alkaline tin bath, and there have been no significant problems reported in running this bath. Since the operation of these plating lines is similar, the quality from plater to plater should be similar.

Alternative Materials and Processes

Session III

Wednesday Morning 11:35

THE ADVANTAGES OF CHLORIDE ZINC PLATING

Edward R. Jorczyk
3M Company
Plating Systems Department
Saint Paul, Minnesota 55101

Pollution problems and the high cost of waste treatment of cyanide zinc electroplating baths has prompted the development of chloride zinc baths. Mirror bright deposits are readily attainable. The chloride bath offers several advantages. Higher efficiencies, thereby liberating less hydrogen at the cathode, enables the chloride bath to deposit more metal in a shorter period resulting in greater production output. Energy savings are realized by lower bath operating voltages. No chelating agents or ammonium ions are present, as in some chloride zinc baths, which could interfere with subsequent waste treatment of other metals in the effluent. Zinc readily plates onto carbonitrided steel, cast and malleable iron out of the chloride zinc bath, which previously required either a cadmium cyanide strike or plated entirely with cadmium. Zinc in this case replaces cadmium, which is more toxic and expensive.

Preceding page blank

The Advantages of Chloride Zinc Plating

by Edward R. Jorczyk
The 3M Company
St. Paul, Minnesota

If there is a voluntary or mandatory reduction in the use of electroplated cadmium because of its toxicity, then there should be suitable alternatives. One of the obvious substitutes is zinc, which is considerably less toxic, less expensive, and readily available. The situations in which zinc may be substituted for cadmium will have to be determined by design engineers and related laboratory evaluations.

Until the last ten years, bright electrodeposited zinc has been primarily plated from cyanide type baths. One can choose from several cyanide zinc[1] bath formulations depending upon the application. A typical 33.7 g/l zinc bath is given in Table 1.

Pollution problems and the high cost of waste treatment of cyanide zinc electroplating baths has prompted the development of alkaline[2], neutral chloride[3], ammonium chloride[4], and the potassium chloride[5] zinc baths. Other types of baths have found only limited acceptance because of poor deposit characteristics, cost, and control problems.

Zinc Substituted For Cadmium

One of the outstanding features of the chloride type baths are their capability of not only plating onto substrates normally plated with cyanide zinc or cadmium, but also onto such substrates as cast iron, malleable iron or carbo-nitrided steel.

These substrates cannot be directly plated with zinc from a cyanide bath. In order to plate zinc from a cyanide bath onto cast iron, malleable iron, or carbo-nitrided steel, the part is first given a thin strike coating of cadmium and then zinc plated to the required thickness. This results in a part with a composite coating of cadmium and zinc. The other choice is to plate the part with cadmium to the specified thickness. Probably at one time or another cadmium has been substituted for zinc on difficult to plate substrates, since visually one looks the same as the other. Since most platers don't know the end use of the parts being plated, the substitution of cadmium for zinc could result in serious complications. Also, the use of a cadmium strike prior to zinc plate usually results in the cyanide zinc bath becoming contaminated with cadmium which codeposits with zinc resulting in dull as well as contaminated deposits.

Types of Chloride Baths

The neutral chloride bath was introduced in 1967[6] and it had two shortcomings. First it was expensive to operate, and secondly,it contained chelating agents which presented problems when they were mixed with waste effluents containing other metal ions. The chelated metals cannot be removed from effluents by conventional means.

The ammonium chloride bath which followed appeared to solve the cost and chelate problem. However, it was quickly found that the ammonium ion from the zinc bath would complex metal ions, such as copper or nickel, if they were present in the effluent, making their removal difficult.

Many countries have restrictions on the amount of ammonium in the effluent that can be discharged into the environment. There are indications that tighter restrictions may be imposed in the future. The ammonium ion increases the nutrient level in aquatic environments and depletes the oxygen supply. In spite of these problems, the ammonium chloride zinc bath has found wide acceptance.

The need of a non-cyanide, non-ammoniated and non-chelated zinc plating process which produces bright leveled deposits led to the development of the potassium chloride bath. It has all the advantages with none of the disadvantages.

Advantages

The advantages of the potassium chloride zinc plating process are:

1. Simplified and low cost waste treatment since ammonium ions, chelates, and cyanide are not present in the bath.

2. High efficiency (95-98%) which can result in energy savings up to 60% with an increase in productivity up to 30% when compared to alkaline processes.

3. Ductile, bright deposits whose appearance resembles bright chromium.

4. Ease of bath control and maintenance.

5. Deposit less susceptible to staining.

6. Difficult to plate substrates readily plated.

7. Deposit readily chromated to impart additional corrosion protection.

Composition And Operating Conditions

A typical composition of the potassium chloride bath is given in Table II.

The operation conditions for this bath are shown in Table III.

Process Cycle

Parts to be plated in the chloride zinc bath generally require better cleaning than is required when plating in a zinc or cadmium cyanide bath. The cyanide baths actually have some cleaning ability to remove organic contaminants such as oil, but this is a poor practice since a plating bath is short lived if contaminated with oil and grease. Pickling must also be adequate because zinc plated from the chloride bath tends to plate over scale. These areas could ultimately blister.

A typical process cycle suitable for plating most ferrous substrates is as follows:

1. Soak clean
2. Anodic electroclean
3. Water rinse
4. Hydrochloric acid pickle, 50% by volume
5. Water rinse
6. Chloride zinc plate
7. Water rinse
8. Chromate dip
9. Water rinse
10. Dry

Two or more rinse tanks may be used between each process tank, and cascading rinse tanks are commonly used to conserve water. Adequate rinsing of parts is very important so that the solution from one process tank is not carried to the next causing contamination. Cleaner dragged into the acid will shorten its life as well as contaminate it with oil or grease. Hydrochloric acid dragged into the plating bath will increase the chloride level to a point where deposits become streaked and pitted and the solution becomes cloudy due to organic "kickout".

Iron Problem

A common problem to chloride zinc baths is that iron increases in the bath and soon reaches a point (250 to 350 ppm) where it acts as a contaminant. The deposit becomes dark and brittle. Iron is introduced from parts being plated, parts that fall off racks and are on the bottom of the tank, drag over of used acid pickle, anodes and replenishment chemicals.

The iron can be kept under control so that it never reaches a point where it is detrimental to the deposit. Iron parts, chips, and burrs that fall to the bottom of the tank should be removed with a magnet on a daily basis; otherwise, they will corrode and contaminate the bath with iron. Daily additions of hydrogen peroxide are made to the bath to precipitate the dissolved iron as ferric hydroxide which is removed by filtration. The hydrogen peroxide (30%) is added each day at a rate of 10 ml of hydrogen peroxide for each 100 liters (1.2 fl.oz. per 100 gallons) of plating solution.

The hydrogen peroxide should be diluted with 4 parts water prior to adding. A properly maintained bath should have iron levels below 75 ppm.

Equipment

Equipment for the ammonium or potassium chloride zinc bath differs from the zinc or cadmium cyanide bath in that corrosion resistant equipment is required.

Since a monetary expenditure is required to purchase new equipment or to convert existing equipment, there is reluctance to change. However, when the plater is faced with capital expenditures to install cyanide waste treatment facilities and the continued expense for chemicals required to treat the cyanide, then costs to change to the chloride system become more attractive.

The cost of converting from a cyanide bath, which consists of two 600 gallon plating tanks having eight stations with 18 by 36 inch barrels has been estimated at $7,895.00.[7]

Tanks - Suitable materials to contact the solution
are PVC, polypropylene, polyethylene, and
some grades of rubber and fiberglass reinforced
plastics.

Filter - Acid resistant components and no metal contact
with the solution.
Turn solution volume over once or twice per hour.
Capable of removing particles 15 micron size and
larger.

Heating and Cooling - Materials of construction may be Teflon* tubes, Teflon coated copper tubing, Titanium coils that are electrically isolated or graphite heat exchangers.

Bus bars - Copper wrapped with vinyl tape or enclosed in PVC tube with contact points exposed for anode or rack contact.

Anodes - Zinc balls or slab meeting ASTM B6-67 "Special High Grade" (zinc - 99.990%).

Racks - Conventional racks coated with insulating coating and stainless steel tips.

Power source - Rack Plating: 6 volts, 5% Max., ripple
Barrel Plating: 12 volts, 5% Max., ripple

Waste Treatment

Effluent from chloride zinc rinse tanks containing 200 ppm zinc can be reduced to at least 0.02 ppm by treating with sodium hydroxide or hydrated lime to raise the pH of the effluent to a range of 9.0 to 9.5. At this pH, the zinc precipitates as a hydroxide and can be removed by filtration, settling, or decantation.

Current cost to treat one pound of zinc chloride is less than $0.15, as compared to $1.10 to $1.50 to treat one pound of zinc cyanide. Cost depends on zinc concentration in the effluent and method of treatment.

---

*Teflon is a registered trademark of DuPont de Nemours Co., Wilmington, Delaware.

M. Rodenkircher[8] reported that the maximum zinc metal concentration found in production plating rinse tanks is generally 200 mg/l; 400 mg/l indicated faulty rinsing practice.

Summary

The potassium chloride bath produces bright ductile zinc deposits economically. It represents a new generation of plating solutions that have minimum impact on the environment because of pollution problems. Energy savings are realized by lower bath operating voltages. Chloride zinc plates readily onto surfaces that formerly required a cyanide cadmium strike prior to cyanide zinc plating or that had to be plated entirely with cadmium.

References

1. E. Leroy Gabel, Plating, 50 (12) 1089 (1963)
2. J. H. Hajdu and J. S. Zehnder, Plating, 58 (5) 458 (1971)
3. "KENBRITE", Product of 3M Co., Pat. No. 3,730,855.
4. "KENLEVEL I", Product of 3M co., Pat No. 3,729,394
5. "KENLEVEL II", Product of 3M Co., Patent Pending
6. K. P. Bellinger, Plating, 56 (10) 1135 (1969)
7. Anon., Product Finishing, 41 (11) 70 (1977)
8. M. Rodenkirchen, Plating, 60 (7) 698 (1973

TABLE I

Typical 33.7 g/l Zinc Bath Composition

$Zn(CN)_2$	60.0 g/l
NaCN	42.0 g/l
NaOH	78.0 g/l
Brightener Additive	Required

TABLE II

Composition of Potassium Chloride Bath*

	Preferred Range	
	Rack	Barrel
Zinc (as metal)	30-34 g/l	18.8-22.5 g/l
Chloride (as chloride)	128-143 g/l	121-128 g/l
Boric Acid	26 - 30 g/l	25 - 28 g/l
Primary Additive	30 ml/l	30 ml/l
Secondary Additive	1.25 ml/l	1.25 ml/l
pH, electrometric	5.0 - 5.5	5.0 - 5.5

*KENLEVEL II, Product of 3M Company, Patent Pending.

TABLE III

Operating Conditions

pH (electrometric)	4.7 - 5.5
Temperature	21° to 32° C.
Agitation	Cathode rod: 1 to 2 meters per minute or gentle air for rack plating only.
Filtration	Continuous: 1 to 2 turnovers per hour
Voltage	Rack: 1 to 3 volts Barrel: 4 to 12 volts
Cathode Current Density	0.1 to 5 A/dm^2
Anode Current Density	Not to exceed 2.5 A/dm^2

The Advantages of Chloride Zinc Plating

by Edward R. Jorczyk
The 3M Company
St. Paul, Minnesota

Typical 33.7 g/l Zinc Bath Composition

$Zn(CN)_2$	60.0 g/l
NaCN	42.0 g/l
NaOH	78.0 g/l

Brightener Additive Required

Types of Bright Non Cyanide Zinc Baths

- Alkaline
- Neutral Chloride (chelated)
- Ammonium chloride
- Potassium chloride

Difficult to Plate Substrates

- Cast Iron
- Malleable Iron
- Carbo-nitrided steel

Shortcomings of Chloride Baths

Neutral Chloride:
- Expensive to operate
- Contains chelating agents

Ammonium Chloride:
- Ammonium complexed
- Nickel and Copper in Effluent

Potassium Chloride Bath

No Cyanide
No Chelating Agents
No Ammonium

Advantages of Potassium Chloride Bath

1. Simplified and low cost waste treatment
2. High efficiency (95-98%)
   Energy savings up to 60%
   Productivity increase up to 30%
   (Comparing to zinc cyanide bath)
3. Ductile bright deposits
4. Bath easy to control
5. Deposit resistant to staining
6. Difficult to plate substrates readily plated
7. Deposit readily chromated
8. Bath easy to control and maintain

Composition of Potassium Chloride Bath*

	Preferred Range	
	Rack	Barrel
Zinc (as metal)	30-34 g/l	18.8-22.5 g/l
Chloride (as chloride)	128-143 g/l	121-128 g/l
Boric Acid	26-30 g/l	25-28 g/l
Primary Additive	30 ml/l	30 ml/l
Secondary Additive	1.25 ml/l	1.25 ml/l
pH, electrometric	5.0-5.5	5.0-5.5

* KENLEVEL II, Product of 3M Company, Patent Pending.

OPERATING CONDITIONS

pH (electrometric)	4.7 - 5.5
Temperature	21° to 32° C.
Agitation	Cathode rod: 1 to 2 meters per minute or gentle air for rack plating only.
Filtration	Continuous: 1 to 2 turnovers per hour
Voltage	Rack: 1 to 3 volts Barrel: 4 to 12 volts
Cathode Current Density	0.1 to 5 A/dm^2
Anode Current Density	Not to exceed 2.5 A/dm^2

Typical Process Cycle

1. Soak clean
2. Anodic electroclean
3. Water rinse
4. Hydrochloric acid pickle, 50% by volume
5. Water rinse
6. Chloride zinc plate
7. Water rinse
8. Chromate dip
9. Water rinse
10. Dry

Iron Contamination

Detrimental to Zinc Deposit

Source: Ferrous Alloy Parts,
Burrs and Chips

Anodes and Chemicals Used
Carryover from Acid Pickle

Iron Removal

Oxidize Soluble Iron (Ferrous) to Insoluble (Ferric) Form and Remove by Filtration.

How: Add 10 ml Hydrogen Peroxide (30%) per 100 liters of Plating Solution on a Daily Basis.

Equipment

Acid Resistant Equipment is Required, which means Capital Expenditures to Modify Existing Equipment or Purchase New Equipment.

Waste Treatment

Treat effluent with sodium hydroxide or hydrated lime to pH 9.5.

Remove precipitated zinc hydroxide.

Clear filtrate should contain less than 0.02 ppm zinc.

Summary

Potassium chloride zinc bath has minimal impact on the environment.

Energy saving realized by lower bath operating voltages.

Replaces cadmium on difficult to plate substrates.

The Advantages of Chloride Zinc Plating

MR. BAYNE: Mike Bayne, Battelle-Northwest. What is the source of your information on that low concentration you find in the effluent?

MR. JORCZYK: That was from laboratory evaluation. Of course, that will vary with industry, because a lot depends upon what else is in the effluent.

MR. COLE: Frank Cole, Republic Steel. What is the function of the potassium chloride? Conductivity?

MR. JORCZYK: It will improve conductivity, of course, and it does add to the grain requirement and overall brightness of the deposit.

MR. COLE: How do you prevent sludging and zinc oxychloride?

MR. JORCZYK: I didn't see any sludging.

SPEAKER: Could you use sodium chloride, or is there a specific reason for potassium chloride?

MR. JORCZYK: It doesn't work as well as the potassium salt, and it is not as conductive.

Alternative Materials and Processes

Session III

Wednesday Morning 12:10

MANGANESE PRESSURE PHOSPHATE COATINGS AS A SUBSTITUTE FOR CADMIUM COATINGS

Henry Crain
Engineering Directorate
Rock Island Arsenal
Department of the Army
Rock Island, Illinois 61201

Rock island arsenal has developed and tested a superior manganese phosphate coating produced under a positive pressure of steam. The pressure phosphate coating has demonstrated salt spray corrosion resistance in excess of 500 hours compared with conventional phosphate coatings having two to four hours salt spray resistance. Pressure phosphate coatings have also exhibited heat resistance to 450°F while still maintaining excellent corrosion resistance. As opposed to the conventional open tank phosphating process, the pressure phosphating process takes place in a closed vessel where the solution and parts are brought to a gage pressure of 1 psi and a temperature of 215°F. With their excellent corrosion protection, pressure phosphate coatings can replace certain metallic coatings, e.g., zinc and cadmium which are not only expensive but present environmental problems. The replacement of conventional cadmium coating on ammunition shim stock by pressure phosphate coatings has been presented as one feasible application of this new process.

MANGANESE PRESSURE PHOSPHATE COATINGS AS A SUBSTITUTE FOR CADMIUM COATINGS

Henry Crain
Engineering Directorate
Rock Island Arsenal
Department of the Army
Rock Island, Illinois 61201

The development of a new and improved manganese phosphating process at Rock Island Arsenal presents a possible alternative coating for cadmium plate. This improved manganese phosphate coating has displayed corrosion resistance of several hundred hours salt spray resistance, a dramatic hundred-fold increase over the salt spray resistance of conventional manganese phosphate coatings. The coating is produced with steam pressures of approximately 1 psi gage to reach bath temperatures exceeding 212°F. Additionally, large quantities of manganese are present in the bath to yield the superior coating. Pressure phosphate coatings have also exhibited heat resistance to 450°F while still maintaining their excellent corrosion resistance. The applicability of this new coating process lies in the corrosion resistance which is comparable to cadmium plate. With cadmium being being scrutinized for detrimental effects on the environment, the improved manganese coatings do offer a possible alternative to cadmium plating. However, applications of this new coating would have to be examined individually and a direct comparison made between the improved manganese phosphate coating and cadmium plate for any particular application.

The paper that follows discusses some of the research and development that was undertaken to develop the process:

INTRODUCTION

Manganese phosphate coatings have been applied to ferrous articles for more than sixty years. The coatings are easy to apply and offer an excellent base for supplementary oil or paint treatment. Specification MIL-P-16232 requires these coatings, without any supplemental treatment, to withstand a 5% salt spray test for one and one half hours.

The conventional manganese phosphate bath contains manganese dihydrogen phosphate $[Mn(H_2PO_4)_2]$, ferrous iron (Fe^{++}), and phosphoric acid (H_3PO_4). The processing temperature range is usually 205°F-210°F. In the process, the basis metal is pickled by the acid at first, and the insoluble manganese phosphate is then precipitated on the metal as a coating.

In recent years, a new and improved manganese phosphate coating has been produced in this laboratory. This new coating is formed by the addition of either manganese tartrate, manganese gluconate, or manganese citrate to the conventional manganese phosphating bath and by processing at temperatures in excess of 212°F under steam pressure. The coating is capable of resisting corrosion for several hundred hours in a 5% salt spray test and displays even greater corrosion resistance after being heated to 450°F for one hour.

Several problems have arisen, however, in attempting to control the continuous production of the superior coatings. In order to solve these problems, this effort was initiated to obtain a better understanding of the underlying phenomena and reaction mechanisms of the modified manganese phosphating process. A previous report* in this same effort has recorded that the primary function of the manganese-organic compounds appears to be in enriching the bath with manganese. The present report details the investigation of the specific concentrations of manganese needed to obtain superior coatings. Since the solubility of manganese compounds are in part determined by the free acid content of the phosphating bath, a study has also been conducted to determine the effect of free acid on baths with high manganese content.

PROCEDURE

An experiment was designed to measure the effect of manganese bath concentration on corrosion protection. The experiment was approached using two different methods to vary the manganese concentration.

One method used a new phosphating solution for each of seven experimental baths. Each bath contained six liters of deionized water, ten milliliters of 85% phosphoric acid, and one of the following amounts of $Mn(H_2PO_4)_2$: 30, 60, 90, 120, 150, 180, and 240 grams. The phosphoric acid corrected the free acid value of the bath to 2.5 points.

---

*Crain, H., "Improved Manganese Phosphate Coatings", GEN Thomas J. Rodman Laboratory Technical Report R-RR-T-6-49-73, July 1973.

The other method used the same six liter bath for all processing runs. Initially the bath contained six liters of deionized water, ten milliliters of 85% phosphoric acid, and 30 grams of $Mn(H_2PO_4)_2$. For each succeeding run, 60 grams of additional $Mn(H_2PO_4)_2$ was added before processing. Manganese carbonate or phosphoric acid were added after each processing period to readjust the free acid value to 2.5 points.

Another experiment was designed to determine the effect of free acid values on corrosion resistance. A series of baths was used for this experiment, each containing six liters of deionized water, 270 grams of $Mn(H_2PO_4)_2$, and one of the following amounts of 85% H_3PO_4: 0, 5, 10, 20, and 30 milliliters.

The specimen panels measuring 2" x 3" x 1/16" were of SAE 1020 steel. Panels were weighed to the nearest milligram before and after processing. Coatings were stripped in chromic acid and the panels were weighed again. These weights yielded the amount of iron etched and coating weights. All processing was done in a pressurized vessel for 30 minutes at 213°F. The gage pressure was always maintained at less than one pound per square inch. Samples of solution were taken from the bath before and after processing. Titrations with 0.1N NaOH were used to determine free and total acid values. Atomic absorption analyses were used to obtain the manganese content.

RESULTS

Table I summarizes the parameters obtained when a series of baths, varying only in $Mn(H_2PO_4)_2$ content, were used to study the effect of manganese concentration on corrosion resistance. The best coatings were obtained with the largest additions of $Mn(H_2PO_4)_2$. The coatings obtained with 30 and

TABLE I

Experimental Parameters For Individual Baths With Fixed Amount of $Mn(H_2PO_4)_2$ Added

Bath #	$Mn(H_2PO_4)_2$ added	Total Acid in points* NaOH	Coating Weight in milligrams per square foot	Salt Spray Corrosion Resistance	Iron Etched in grams per panel	Manganese Concentration In %
1	30 grams	9.6	2,580	1 hour	0.488	0.070
2	60 grams	14.8	1,300	1 hour	-----	0.126
3	90 grams	18.2	1,480	2 hours	0.120	0.178
4	120 grams	22.8	2,470	2 hours	0.106	0.226
5	150 grams	27.6	4,940	8 hours	0.088	0.275
6	180 grams	31.4	7,260	56 hours	0.078	0.300
7	240 grams	40.2	8,340	31 days	0.070	0.382

*** One point equals one milliliter of 0.1N NaOH per 10 milliliters of sample.**

60 grams of $Mn(H_2PO_4)_2$ were inferior, failing the 5% salt spray test in less than one hour. Coatings produced in baths having 90, 120, and 150 grams of $Mn(H_2PO_4)_2$ appeared similar to conventional manganese phosphate coatings.

Figure 1 shows manganese content in weight percent versus salt spray resistance in hours. An inflection point is noted in the curve at approximately 0.27% manganese. Above this concentration, the coatings display superior corrosion resistance.

Figure 2 shows coating weight versus salt spray resistance. The curve is similar to the one in Figure 1 and yields an inflection point at approximately 0.50 grams coating weight. Above this point, the coating provides superior corrosion resistance.

The data and plots obtained from the continuous bath experiment, in which increments of $Mn(H_2PO_4)_2$ were added after every processing run, are similar to the experiment just discussed. An example of this similarity is shown in Figure 3. In this plot, the salt spray resistance versus manganese content curve displays an inflection point at approximately 0.30% manganese.

Table II summarizes the data obtained in the free acid experiment in which varying amounts of 85% H_3PO_4 were added to the phosphating baths. The poorest coatings were produced with 30 milliliters of H_3PO_4, while the best coatings were produced with 5 and 10 milliliters of H_3PO_4. In Table II, note that the difference between the initial and final manganese bath concentrations decreased as the amount of phosphoric acid was increased.

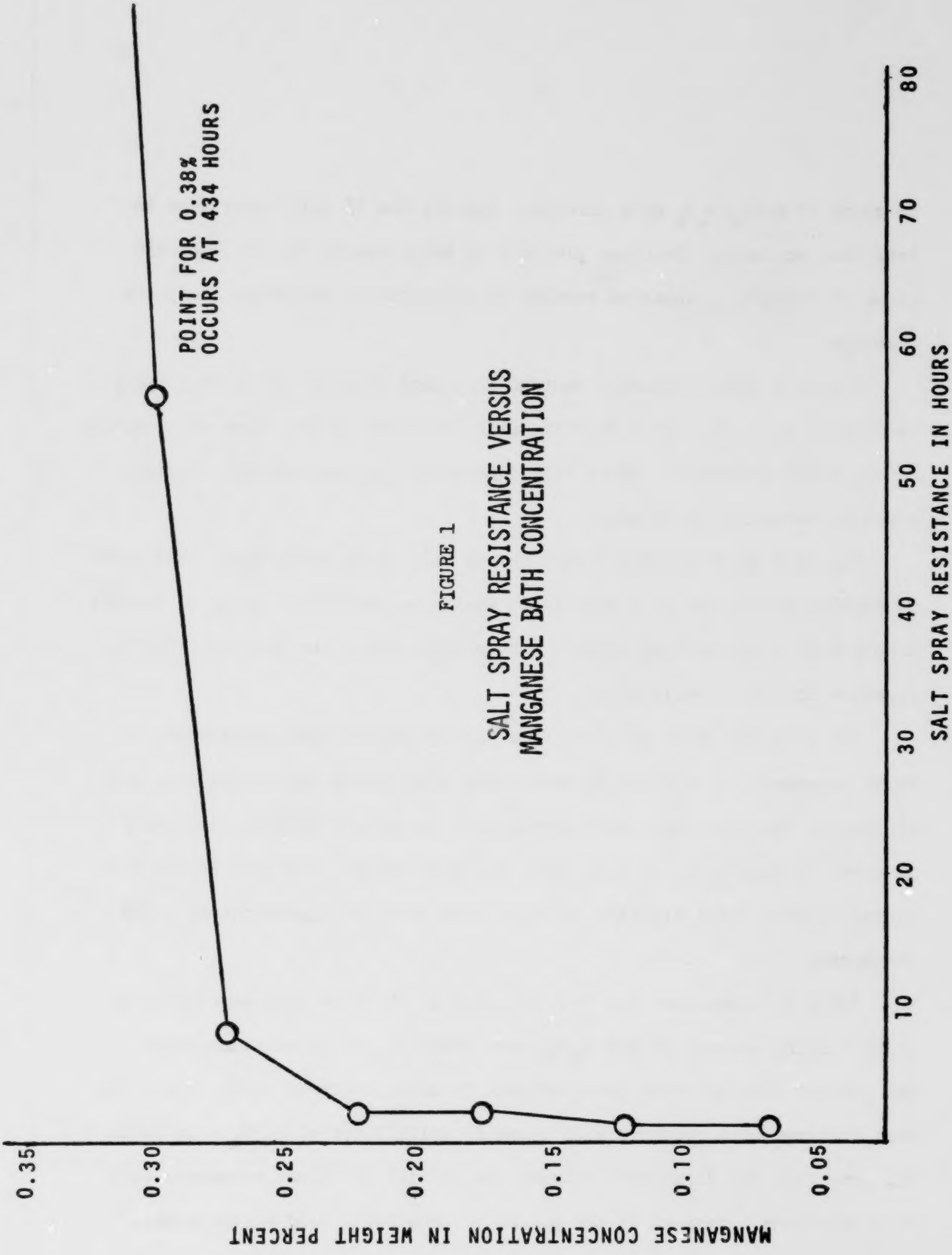


FIGURE 1

SALT SPRAY RESISTANCE VERSUS
MANGANESE BATH CONCENTRATION

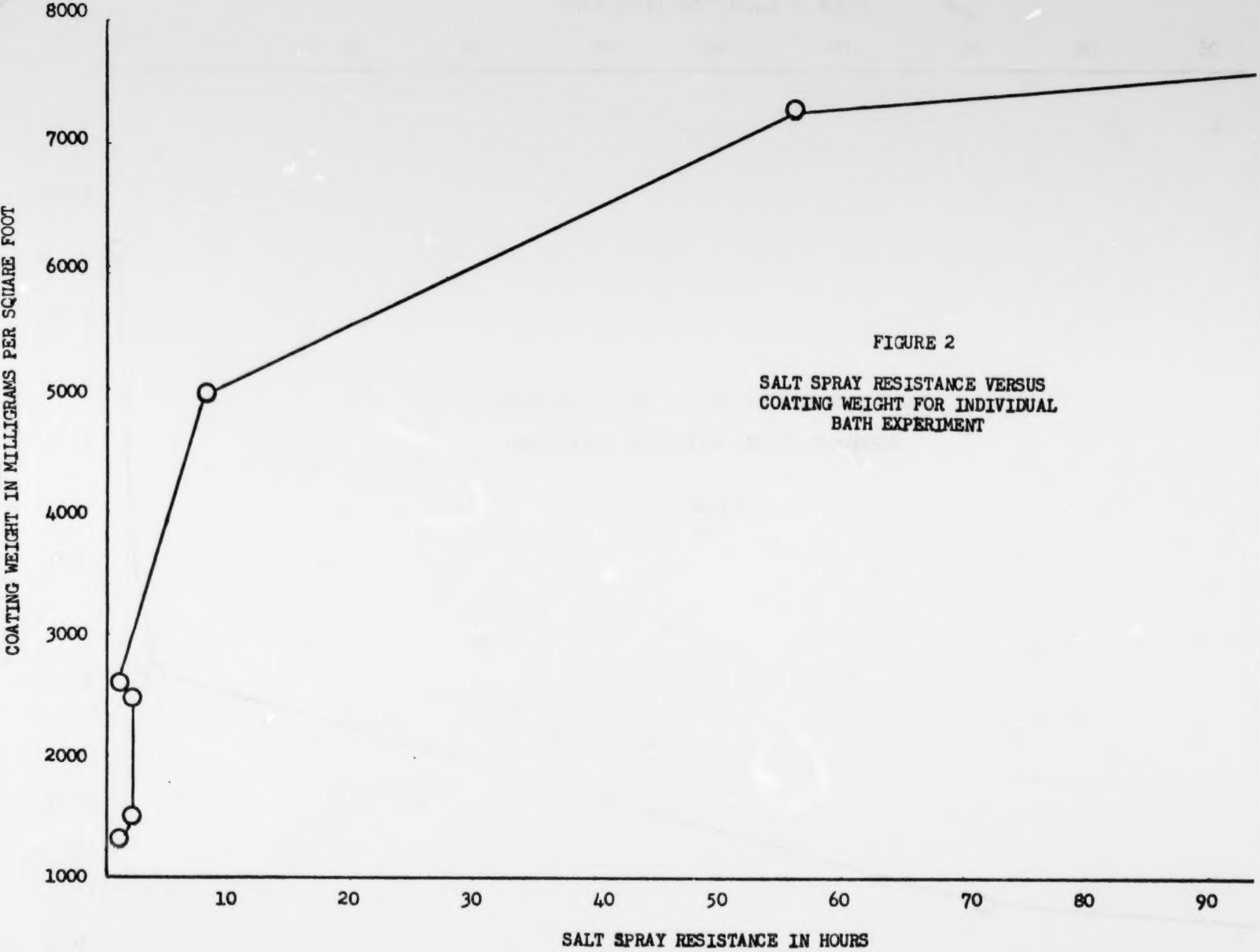


FIGURE 2

SALT SPRAY RESISTANCE VERSUS COATING WEIGHT FOR INDIVIDUAL BATH EXPERIMENT

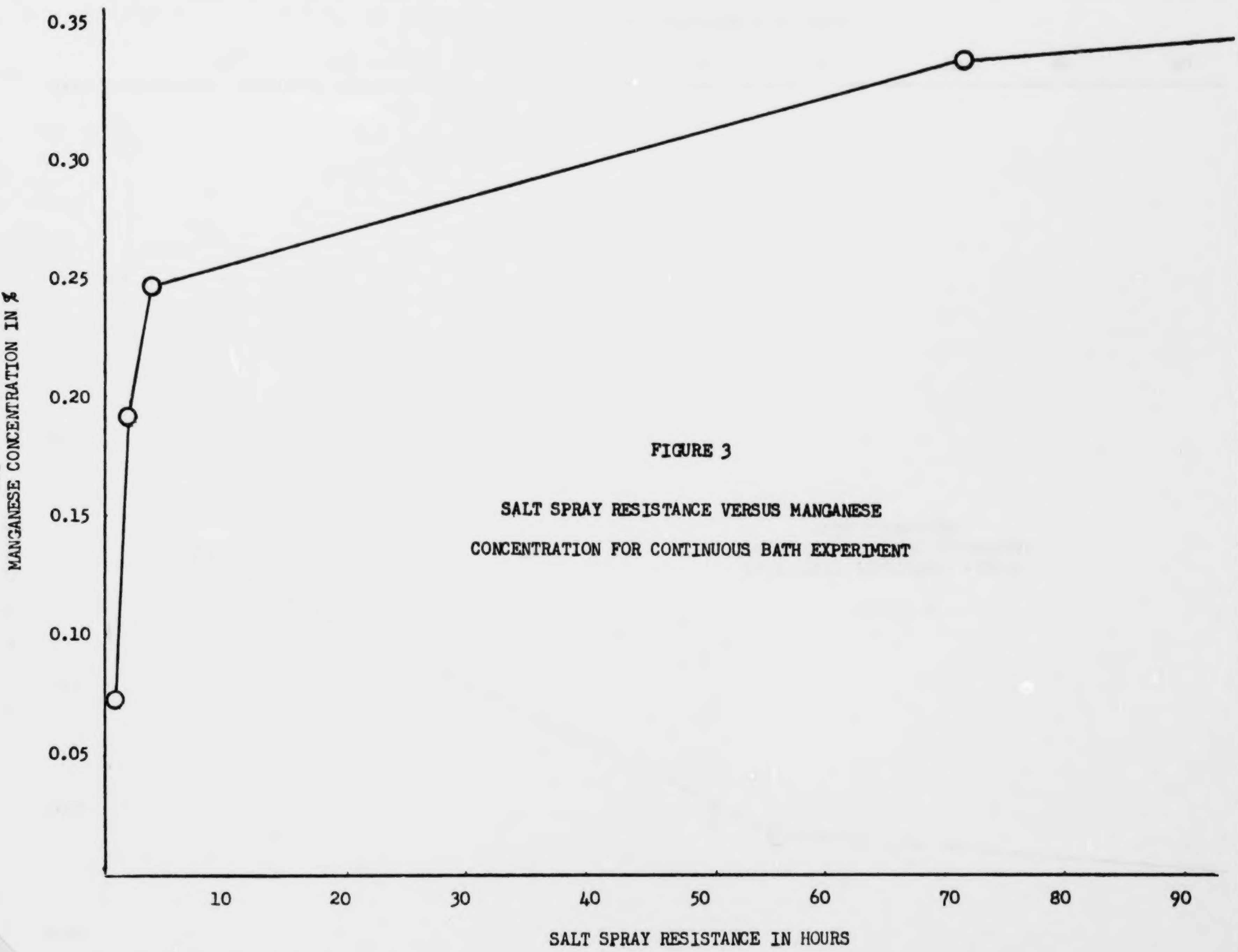


FIGURE 3

SALT SPRAY RESISTANCE VERSUS MANGANESE CONCENTRATION FOR CONTINUOUS BATH EXPERIMENT

TABLE II

Experimental Parameters For Free Acid Study.

Bath #	Amount of H_3PO_4 added	Coating weight in milligrams per square foot	Free acid in points*	Salt spray corrosion resistance	Manganese content in % (before processing)	Manganese content in % (after processing)	Difference between initial and final %
1	0 ml.	6,190	1.0	30 hours	0.47%	0.35%	0.12%
2	5 ml.	7,730	2.2	100 hours	0.45%	0.36%	0.09%
3	10 ml.	7,510	3.6	100 hours	0.46%	0.38%	0.08%
4	20 ml.	8,570	4.6	36 hours	0.47%	0.42%	0.05%
5	30 ml.	4,270	6.5	4 hours	0.47%	0.45%	0.02%

* One point equal one milliliter of 0.1N NaOH per 10 milliliters of sample.

A plot of this difference is illustrated in Figure 4.

DISCUSSION

The experimental data, derived from studies of varying the manganese bath concentration, clearly show the great importance of manganese content in producing superior coatings. The critical points in the plots of manganese concentration versus salt spray resistance indicate the value at which the coatings become better than conventional coatings. Coatings having several hundred hours of salt spray resistance can be produced with baths having manganese concentrations slightly higher than the critical values.

In the experiments mentioned in this report, phosphating baths have been enriched with manganese by adding additional $Mn(H_2PO_4)_2$. In previous testing, Wagner* of this laboratory has accomplished the manganese enrichment by adding manganese organic compounds such as manganese tartrate, gluconate, and citrate. He added 10 grams per liter of these compounds to a conventional bath. He thus succeeded in exceeding the critical manganese value and produced superior coatings. The main function of these compounds can be stated as manganese enrichment. Any manganese compound can be used for this purpose as long as the anionic part of the compound is not detrimental to the bath.

The increase in manganese bath content is linked to heavier coatings. Larger amounts of manganese result in larger amounts of $Mn_3(PO_4)_2$ being formed and deposited as heavy crystalline coatings. The heavier coatings

---

*Wagner, L. H., unpublished technical report, GEN Thomas J. Rodman Laboratory.

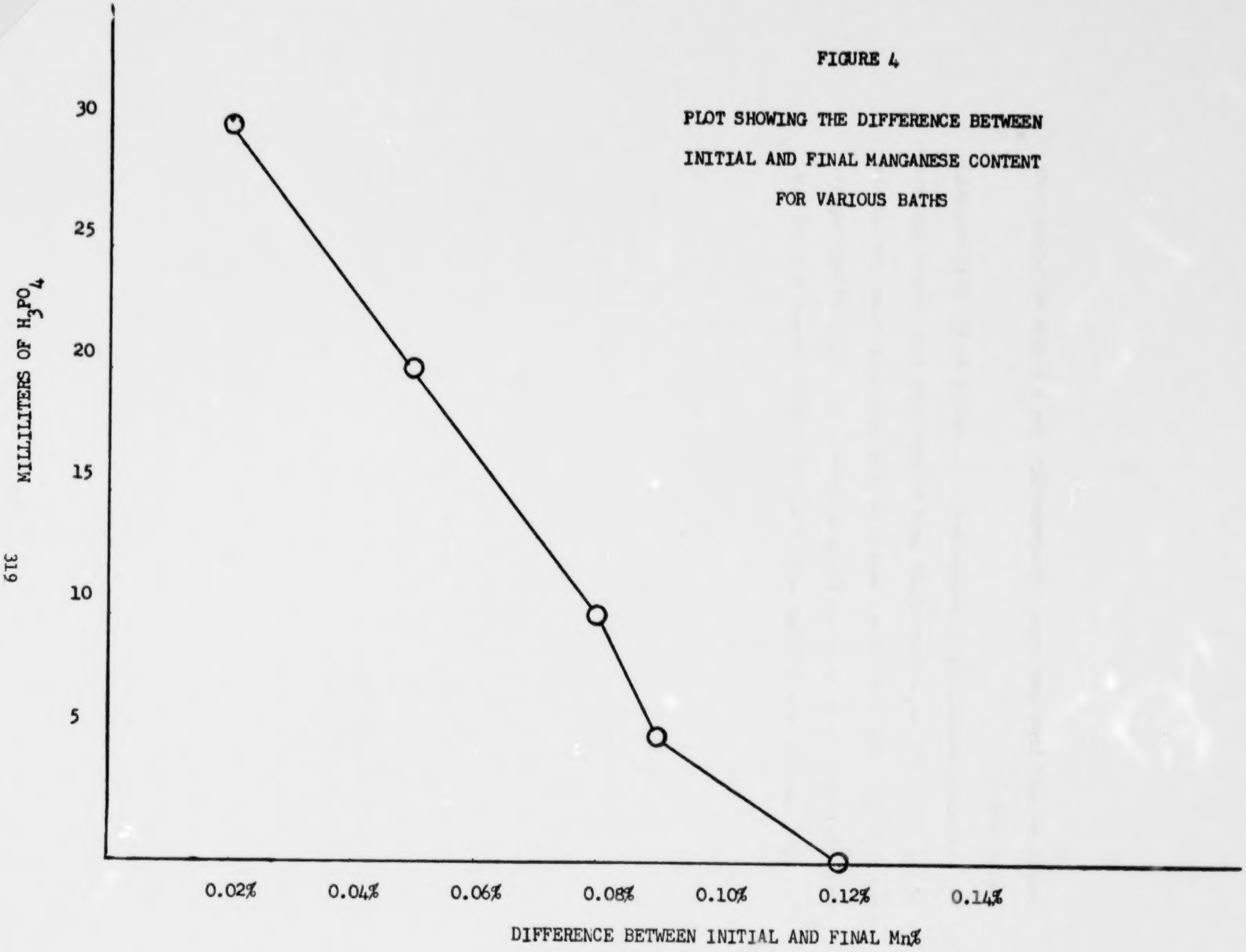


FIGURE 4

PLOT SHOWING THE DIFFERENCE BETWEEN INITIAL AND FINAL MANGANESE CONTENT FOR VARIOUS BATHS result in less free pore area. Consequently, the coatings withstand corrosion better.

Manganese solubility is determined to an extent by the acid condition of the bath. The experiment which used various free acid values demonstrates that high free acid values result in less manganese being precipitated from solution. Thus, less $Mn_3(PO_4)_2$ is formed, and thin coatings appear. The best coatings are obtained with free acid values between 2.0 and 4.0.

Manganese Pressure Phosphate Coatings as a Substitute for Cadmium Coatings

MR. TUTTLE: Jim Tuttle, Rust Proofing and Metal Finishing Corporation. In the specification you mentioned, MIL-P-16-232, you were working with Type M, Class 1, which has one and a half hour salt spray requirement. Under that same spec, Type M, Class 4 is a treatment with an inorganic salt and the salt spray resistance is elevated to 24 hours. Have you tried treating this new phosphate with the inorganic salt?

MR. CRAIN: No, we haven't.

MR. TUTTLE: I think that would be very interesting and worthwhile.

MR. CRAIN: Right. As a matter of fact, there are several areas that we still can investigate. As I mentioned, this improved corrosion resistance up to several thousand hours is without any supplemental treatment at all. That does not include the chromate post-treatments. It might extend up to 5,000 or 10,000 hours, but we have not looked at that yet.

MR. TUTTLE: Treatment with this Class 4 inorganic salt improves the heat resistance of the manganese phosphate a great deal so that it will pass the requirements after being heated to 500 degrees fahrenheit. This is not reflected in the spec.

MR. LAURILLIARD: John Laurilliard, Standard Pressed Steel. With your high coating weights, 8,000 milligrams per square foot, what kind of coating thickness do you get? What kind of build-up?

MR. CRAIN: Conventional manganese phosphate coatings usually have two to six ten-thousandths of an inch coating thickness. This improved phosphating process will give coatings approximately five times this, so we are talking about one-thousandth of an inch.

MR. LAURILLIARD: During the processing, building up the heavy coatings, is there any consumption or etching of the base metal?

MR. CRAIN: In one slide I have the amount of iron that was being etched. The low coating weights that are comparable to conventional manganese phosphating have more iron being etched, on the order of four or five times more. With the heavy coating weights, we would have very little iron being etched.

MR. LAURILLIARD: This could be detrimental to high strength fatigue-rated materials; increased etching can reduce fatigue.

MR. CRAIN: Well, we have reduced etching for the new process.

MR. LAURILLIARD: How about hydrogen embrittlement? Do higher coating weights cause more hydrogen embrittlement?

MR. CRAIN: We have not run tests, and in everything that we have looked at, the new coating seems to have the same properties of the conventional manganese phosphate.

I would expect the hydrogen embrittlement problem to be the same. There is a baking treatment described by MIL P-16-332 that would have to be used with this coating.

MR. LAURILLIARD: On one of your last slides, your last data point at 7,000 milligrams per square foot showed 60 or 70 hours.

MR. CRAIN: The last point on the graph could not be presented on this slide. As I mentioned, it would be far out on the curve. The 7,000 milligrams per square foot was something like 56 hours.

MR. LAURILLIARD: Do you have any corrosion data on production pieces, or only on test panels?

MR. CRAIN: We have only tested two by three inch panels of low carbon 1020 steel. Recently we have been processing some fasteners, but we don't have the results on these yet.

MR. LAURILLIARD: Were these tumbled?

MR. CRAIN: No, they weren't tumbled. They were suspended. In a system that the Army is going to try to set up, they are going to use tumbling.

MR. LAURILLIARD: Do you get the same type of results on grit-blasted parts as you do on those that aren't? The latest revision on the spec doesn't make it mandatory that parts be grit-blasted.

MR. CRAIN: It has always been my experience that grit-blasting is quite essential to the quality of the phosphate coating. I have noticed when grit-blasting was not performed that the coatings were of a poor quality.

The quality of this improved phosphate coating will be reduced if the specimen is not properly grit-blasted.

MR. LAURILLIARD: Don't you think that there are more parts being phosphated that are not grit-blasted?

MR. CRAIN: In our shop, we have a series of grit-blasting machines varying the size of the grit. We get the best results when parts are grit-blasted with number 80 grit. As a finer finish is required and finer grit is used in the blast, the quality of the phosphate coating seems to decrease.

MR. LAURILLIARD: Do you find any difference with the non-steel grit like aluminum oxide?

MR. CRAIN: The steel grit is better than aluminum oxide. It imbeds steel particles into the piece being plated that promote the deposition of the manganese phosphate so that you get a better coating. The aluminum oxide, of course, will not do this. The iron forms the bonding between the coating and the specimen. If there is more aluminum oxide, you are not going to obtain that bond or the same quality of the coating.

MR. BLESS: Mike Bless, Naval Air Engineering Center, Lakehurst. Do you intend to produce a specification to cover the new process?

MR. CRAIN: I don't know what plans are being made for that. I know I am not going to be involved. The people at Picatinni Arsenal are currently in charge of this project, but I suppose a specification would definitely have to be written.

MR. BLESS: Since we are not a manufacturer, the only access we could have to it is by calling out a specification of some sort.

Alternative Materials and Processes

Session IV

Wednesday Afternoon 1:45

EFFECTS OF CADMIUM ON FISH AND WILDLIFE

Calvin M. Menzie
Division of Habitat Preservation Research
Fish and Wildlife Service
Department of the Interior
Washington, D.C. 20240

Cadmium, produced as a metal refining by-product, passes into the aquatic environment in effluents from pesticides and metal industries - extraction, refining, machining, electroplating and welding. Studies have shown that this material can then be accumulated by some aquatic organisms to a significantly higher level than occurs in the aquatic environment. Analyses have also shown that levels of cadmium in muscle of finfish is lower in deep-water fish then in fish taken in coastal waters.

Bioassays have been used to determine acute toxicity of cadmium compounds to various marine species. Exposure of successive generations of brook trout to cadmium has shown that low concentrations can adversely affect growth and reproduction.

Studies with small mammals such as rabbits indicated that cadmium exhibits a variety of physiological effects that include enlarged spleen and heart and fatty degeneration of liver and kidneys as well as some hematological effects.

Preceding page blank

Effects of Cadmium in the Environment

Calvin M. Menzie
Fish and Wildlife Service
Department of the Interior
Washington, D.C. 20240

Cadmium is an ubiquitous chemical (Tables 1-8) in aquatic and terrestrial ecosystems (Anderson et al., 1974; Blaylock et al., 1973; Bondietti et al., 1973). Although some marine species have the ability to concentrate cadmium above very low levels, there does not appear to be evidence of cadmium concentration in marine food chains. The potential, however, does exist. Cadmium concentrations appear to be highest in shoreline sections of contaminated areas. Deep sea sediments of the North Atlantic averaged only about 0.2 ppm (Aston et al., 1972). In the Mississippi-Missouri River systems, analyses indicate that mine drainage may be the source of cadmium (Fleischer et al., 1974). A close association has been noted between proximity to heavy urbanization and metal concentration in growing oysters (Ratkowsky et al., 1974).

Mammals

Cadmium, in addition to implication in hypertension and arteriosclerosis, has been found to accumulate in humans in kidney tissue. In experiments with rabbits, oral and parenteral administration of cadmium has resulted in arterial hypertension and inhibition of vasopressor responses (Thind et al., 1970). Studies have also shown that cadmium was deposited in kidney and liver of rabbits

TABLE I. Samples collected in vicinity of a deep water dump site in the Middle Atlantic Bight*.

	(ppm, wet wt)			
	Muscle	Liver	Whole Animal	Gills
Antimora rostrata	<0.12	0.33		
Nematonuras armatus	0.11	1.27		
Halosauropsis macrochir	<0.12			
Synaphobranchus kaupi	0.12			
Geryon quinquedens	<0.10			0.81
Seriola sp.	<0.10	0.24		
Hygophum sp.			0.09	
Stephanolepsis hispidus			0.13	

*Sediments also taken from deep water dumpsite in New York Bight--analyses of 9 samples each taken on a different date or at a different location. Cd = 1.25 ppm (dry wt) for all nine (Greig et al., 1976).

TABLE 2. Concentration of cadmium in fish tissues (ppm wet wt)
(Northumberland Coast of England)

	Tissue								
Species	Gill	Axial Skeleton	Skin	Stomach Wall	Liver	Fat	Kidney	Muscle	Gonad
Lumpsucker			1.7	0.6	1.08	0.82	1.83	0.12	
Sprat			0.8					0.24	
Coal Fish	3.2	1.3	3.1	2.1			4.2	0.64	
Plaice	0.8		1.3	3.9	2.9			1.4	
Young Cod	1.2	1.3	3.5	0.6	1.7			1.3	
Viviparous Blenny		0.8	1.9	1.0	0.4			0.3	1.6
Dab		0.47	0.26	0.36	1.38		0.2	0.18	0.09
Cod		0.25	0.4	0.1	0.06	0.17	0.99	0.1	0.09

(Wright, 1976)

TABLE 3. Cadmium in dressed Canadian fish (ppm wet wt)

Species	Source	Concn.
Lake white fish (Coregonus clupeaformis)	Moose L.	0.05
	L. Ontario	0.05
Northern pike (Esox lucius)	Moose L.	0.05
	L. St. Pierre	0.05
	L. Erie	0.05
Rainbow smelt (Osmerus mordax)	L. Erie	0.06
Yellow perch (Perca flavescens)	L. Erie	0.05

(Uthe and Bligh, 1971)

TABLE 4. Cadmium in Great Lakes fish (ppm wet wt)

Species	Liver
Herring	1.6
Bloater	0.09 & 0.3
Whitefish	0.4 & 0.7
Round whitefish	0.4
Lake trout	0.07 & ≤3
Smelt	0.07
Goldfish	1.4
White bass	0.2
Yellow perch	0.54
Walleye	0.2
Grand Average	0.4

(Lucas et al., 1970)

TABLE 5. Cadmium in organisms from the Irish Sea (ppm dry wt)

Coelenterates	
Tealia felina	0.66
Alcyonium digitatum	4.1
Echinoderms	3.7
Asteria rubens	5.3
Solaster papposus	4.5
Porania pulvillus	9.4
Henricia sanguinolenta	3.5

(Riley and Segar, 1970)

TABLE 6. Cadmium distribution in water from Florida Everglades

Source		g/liter water
South Florida Canal -	Undeveloped Area	0.4
	Developed Area	2.8
Everglade estuaries		
Lostman's Bay		1.4
Chokoloskee Bay		4.2

Highest concentration cadmium in Barron River canal occurred in the portion of canal adjacent to cultivated areas.

Chokoloskee Bay receives direct discharge from the canal.

Lostman's Bay has a natural drainage without an obvious artificial source for heavy metals.

(Horvath et al., 1972)

TABLE 7. Cadmium in marine animals from Bristol Channel samples (ppm)

Species	Range
Fucus vesiculosus	2 to 75
Patella vulgata	9 to 500
Mytilus edulis	4 to 60
Nucella lapillus	31 to 725
Littorina littorea	8 to 75

(Nickless et al., 1972)

TABLE 8. Cadmium in marine organisms from Somerset coast of England

Species	Conc. (ppm wet wt)	
	Range	Av.
Limpet (Patella vulgata)	10.3 to 118.5	
controls	0.9 to 13.9	6.4
Crab (Carcinus maenas)	14.3 to 33.1	22.4
(Cancer pagurus)	----	5.0
Lesser Blackbacked gull eggs		0.06
Herring gull eggs	0.03 to 0.06	---
Dog whelk	16.3 to 39.0	24.0
(control)		2.2
Cod (3 yrs old)	0.26	
(2 yrs old)	0.12	
Dogfish	0.07 to 0.59	
Flounder	0.68 to 1.67	
Grey Mullet	0.08	
Pollack	0.46	
Rockling	0.06	
Skate	0.47	
Whiting	0.09	
Thronback Ray	0.10	
Shrimp - cooked	0.29	
- raw	0.39	

(Peden et al., 1973)

that received cadmium chloride for 6 to 7 months by subcutaneous injection (Piscator and Axelsson, 1970). Histological examination showed signs of damage to renal tubules and blood tests revealed hemolytic anemia and plasma protein changes (Axelsson and Piscator, 1966a and b; Axelsson et al., 1968). In other studies, tissues of hypertensive rabbits had significantly higher cadmium levels than was present in tissues from control animals. Within the hypertensive group, kidney and liver contained the greatest cadmium level, followed by mesenteric artery, aorta and heart in that order. No significant difference in water content between hypertensive and normal tissues was observed (Fischer and Thind, 1971). Using aortic strips from normal rabbits, it was observed that cadmium produced a dose-related but reversible inhibition of epinephrine, norepinephrine and angiotensin responses (Thind et al., 1970).

In vitro studies indicated that steroid biosyntheses were altered in the gray seal (Halichoerus grypus) (Freeman and Sangalang, 1977).

Birds

Mallard ducks (*Anas platyrhynchos*) were fed amounts of cadmium varying from approximately 2 ppm to 200 ppm. At 2 and 20 ppm cadmium, no appreciable renal damage was observed; at 200 ppm, after 60 and 90 days of treatment, interstitial nephritis, tubular degeneration, and tubular necrosis was seen. Kidney weights also increased significantly. At 20 ppm, there was induction of some alterations in testes of birds. Severe lesions were produced at 200 ppm; testes had atrophied after 90 days treatment and the spermatogenic process ceased (White et al., in press).

Japanese quail (Coturnix coturnix) were fed diets containing 75 mg/kg cadmium for 4 weeks. In addition to severe anemia, low iron and high cadmium levels in liver, some retardation of growth also occurred. Addition of ascorbic acid to the diet decreased the toxic effects of cadmium (Fox and Fry, 1970).

When sparrows were fed ^{109}Cd-tagged seed, the amount of Cadmium assimilated was about 6% of that available and was not concentrated above the food source level. The half-life was relatively long and 64% of the body burden (not including the gut) was found in the kidney and liver (Fassett, 1975).

AQUATIC ORGANISMS

Fish

Zebra fish (Brachydanio rerio) were fed fish food containing 10 ppm Cadmium as cadmium acetate. Uptake plateaued at about 15 µg/g (dry wt) in females after about 4 months and at about 5 µg/g (dry wt) in males after about 2.5 months. The monthly total number of eggs produced began to decline after the first month (Rehwoldt and Karimian-Teherani, 1976).

Livers from killifish (Fundulus heteroclitus) were used to assess the effects of cadmium on five enzymes (Table 9) (Jackim et al., 1970).

TABLE 9. Percentage enzyme inhibition by cadmium

Enzyme	Molar concn	% Inhibition
Alkaline phosphatase	10^{-7}	1
	10^{-6}	27
	10^{-5}	72
	10^{-4}	80
Acid phosphatase	10^{-2}	11.5
Xanthine oxidase	10^{-4}	N.E.
Catalase	10^{-4}	1
	10^{-3}	12
RNAase	10^{-4}	12.6

Goldfish (Crassius auratus), when exposed to 380 µg Cd/l for 30 days, exhibited deviations in plasma sodium and chloride levels and in sodium, potassium, chloride and water content of tissues (McCarty and Houston, 1976).

Adult bluegill (Lepomis macrochirus) were exposed to cadmium for 11 months. Highest tissue residues were found in liver, intestine and caecum, and kidney. At 31 µg/l no adverse effects were observed. At 80 µg/l chronic effects occurred. Mortality was related to concentration. At 239 µg/l, onset was the same as at 80 µg/l but subsequent mortality was higher at the 239 µg level. Spawning was erratic. Development of embryos appeared normal at the lowest level tested. At 80 µg/l, some embryos developed severe abnormalities. At the higher levels of exposure, nearly all embryos developed abnormalities, including pericardial and abdominal edema, delayed yolk sorption, shortened and deformed caudal fin and peduncle, microcephalia and lordosis dorsally of more than 90 from normal (Table 10) (Eaton, 1974).

TABLE 10. Chronic effects of cadmium on bluegill

	Mortality		Spawning	
Cd concn. (μg/l)	On-set	100%	No.	Deformed larvae
2140	141 days	264 days	2	+++
757	6 mos.	9 mos.	0	+++
239	8 mos.		4	+++
80	8 mos.		24	+
31	(no mortality)		5	0
0	------		9	

In studies with catfish (Ictalurus punctatus), biomagnification of cadmium was inversely related to exposure concentration in liver and kidney (Table 11) (Smith et al., 1976).

TABLE 11. Biomagnification of cadmium in catfish

Exposure level (ppm)	Biomagnification by liver	Biomagnification by kidney
0	----	----
50	12 x	41 x
100	6	15
200	4	15
400	3	6
800	2	5

In order to evaluate the possible changes in toxicity of cadmium, eggs of autumn spawning Baltic herring (Clupea harengus) were incubated in contaminated waters at varying salinity. Embryonic survival was dependent on the salinity and deleterious effects were more evident in brackish water than in sea water. Activity of the embryos decreased with decreasing salinity. Embryo survival was greater at high salinity than at low salinities. Hatching rates were good at all cadmium-salinity combinations, but incubation time shortened with increasing cadmium concentration. Viable hatch was unaffected at salinities of 16 o/oo to 32 o/oo and cadmium concentrations up to 0.5 ppm. At 0.5 ppm cadmium and 5 o/oo salinity, there was only 1% viable hatch. At 5ppm cadmium, there were no viable larvae. With increasing cadmium concentration, length of newly hatched larvae decreased and yolk sac volumes increased. Cadmium content of eggs was higher in lower salinities (Table 12) (von Westernhagen et al, 1974).

TABLE 12. Effect of cadmium and salinity on herring eggs

	Embryonic survival until hatching, %				50% Hatching, days				% Viable hatch			
Salinity, o/oo	5	16	25	32	5	16	25	32	5	16	25	32
Cd, ppm												
0					13	13	13	12				
0.1	95	92	95	67	12	13	13	13	88	97	98	96
0.5	85	92	95	67	12	12	13	12	0	96	98	98
1.0	90	90	99	58	12	11	11	12	0	60	97	97
5.0	21.7	32.8	54.9	51.0	14	12	12	10	0	0	0	0

When 3 generations of brook trout (Salvelinus fontinalis) were exposed to cadmium, a significant number of first and second generation adult males died at 3.4 μg/l during spawning. Growth of second and third generation offspring was significantly retarded. As in other fish exposed to cadmium, kidney, liver and gill tissue accumulated the greatest amounts of cadmium (Benoit et al., 1976; Rowe and Massaro, 1974; Kumada et al., 1973).

When exposed to cadmium levels of one to 25 ppb, 3-4 year-old brook trout exhibited testicular injury and changes in androgen synthesis. At 25 ppb, testis of fish showed marked discoloration with dark purple-brown patches randomly scattered. At 10 ppb of cadmium, abnormally vascularized discolored testis were seen in seven of eight fish. Histological examination also revealed extensive hemorrhagic necrosis. Histochemical studies indicated a reduction of lipid material in the lobule-boundary cells of damaged testes and no regeneration of Leydig cells, the probable site of steroid production in brook trout. *In vitro* studies with tissues from mid-testes of control fish and fish exposed to 25 ppb cadmium showed synthesis of 11-ketotestorone (11-KT) from 4-^{14}C-pregnenolone in control but not in Cd-damaged tissues. Altered biosynthesis of other unidentified compounds was also indicated by X-ray autoradiography of chromatograms (Sangalang and O'Halloran, 1972).

Rainbow trout (*Salmo gairdnerii*) respond slowly to cadmium poisoning. In a continuous flow system, with 290 mg/l $CaCO$ and ambient temperature 11.0-12.5C, data suggested a 7-day TL_m between 0.008 to 0.01 mg Cd/l. Preliminary tests in soft water indicated a 7-day TL_m of about 0.01 mg Cd/l (Ball, 1967).

Fathead minnow (*Pimephalas promelas*) were exposed to varying concentrations of cadmium. The data indicated that 57 μg Cd/l decreased survival of developing embryos and that mortality occurred during the last three days of incubation. Many of the hatched fish were inactive and deformed. In some the heart was beating but RBC was not circulating. In others, there were many blood clots throughout the vascular system. At 4.5 to 37 μg Cd/l, no adverse effects on survival, growth or reproduction was observed (Pickering and Gast, 1972).

The common mummichog (*Fundulus herteroclitus*), when exposed to 50 ppm cadmium (30 o/oo salinity, pH 7.8, 20C, and 7 mg O /l), showed changes in the intestinal tract, in the kidney, and in the blood. Eosenophils rose from 3% (in controls) to an average of 43% (in exposed fish). Intestinal lesions occurred after one hour of exposure; kidney lesions, after 8 hours (Gardner and Yevich, 1969).

Mixtures of cadmium, copper and zinc salts were more toxic than expected on the basis of individual salts. Cadmium, at concentrations not usually lethal, decreased survival of mummichogs that had been intoxicated by salts of copper, zinc or both. Residues in survivors held in cadmium-containing mixtures did not conform to patterns of single elements (Eisler and Gardner, 1973). When mummichogs were exposed to 50 ppm cadmium alone, pathological changes attributable to cadmium poisoning were observed in the intestinal tract, the kidney and gills. The observed effects resemble pathological changes demonstrated experimentally in animals and clinically. Changes among eosinophilic cells were also indicated (Gardner and Yevich, 1970).

Exposure of the cunner (*Tautogolabrus adspersus*) to varying cadmium concentrations affected blood serum osmolality and gill tissue oxygen consumption. At a level of 48 ppm, abnormally high serum osmolality occurred; at a level as low as 3 ppm, the normal rate of oxygen consumption was reduced (Thurberg and Dawson, 1974). Histopathological effects, after acute exposure (48 ppm and 96 h) to cadmium

TABLE 13. Toxicity of cadmium to marine species

Species		LC (µg/l)		Reference
		96 h		
Opossum shrimp	(*Mysidopsis bahia*)	15		Nimmo et al, in press
Amphipod	(*Austrochiltonia subtenius*)	40		Thorp and Lake, 1974
Freshwater shrimp	(*Paratya tasmaniensus*)	60		Throp and Lake, 1974
Stickleback	(*Gasterosteus aculeatus*)	200		Jones, 1939
Hermit crab	(*Pagurus longicarpus*)	320		Eisler, 1971
Sand shrimp	(*Crangon septemspinosa*)	320		" "
Grass shrimp	(*Palaemonetes vulgaris*)	420		" "
		760	120^1	Bahner and Nimmo, 1975 Nimmo and Bahner, in press
Common starfish	(*Asterias forbesi*)	820		Eisler,1971
Juvenile bay scallop	(*Argopecten irradians*)	1480		Nelson et al., 1976
Common soft-shell clam	(*Mya arenaria*)	2200		Eisler, 1971
Pink shrimp	(*Pinaeus duorarum*)	3500	718^2	Bahner and Nimmo, 1975 Nimmo and Bahner, in press
Green crab	(*Carcinus maenus*)	4100		Eisler, 1971
Mud crab	(*Eurypanopeus depressus*)	4900		Collier et al., 1973
Atlantic oyster drill	(*Urosalpinx cinerea*)	6600		Eisler, 1971
E. mud snail	(*Nassarius obsoletus*)	10500		" "
Sandworm	(*Nereis virens*)	11000		" "
Yellow-eye mullet	(*Aldrichetta forsteri*)		14300^3	Negilski, 1976
			15500^4	" "
Small-mouthed hardyhead	(*Atherinasoma microstoma*)		14600^5	" "
Striped killifish	(*Fundulus majalis*)	21000		Eisler, 1971
Blue mussel	(*Mytilis edulis*)	25000		" "
Sheepshead minnow	(*Cyprinodon variegatus*)	50000		" "
Mummichog	(*Fundulus heteroclitus*)	55000		" "

[1] 29 days
[2] 30 days
[3] 120 h
[4] 58 h
[5] 168 h

TABLE 14. Toxicity of cadmium to aquatic insects

	µg/l	Days	% Survival
Diptera			
Atherix variegata	10,000	21	100
Hexatoma sp.	10,000	21	80
Holorusia sp.	42,500	7	50
Ephemeroptera			
Ephemeopteran nymph	84	4	50
Ephemerella grandis grandis	42,500	7	0
Ephemerella grandis grandis	28,000	4	50
Plecoptera			
Acroneuria pacifica	17,500	21	10
Arcynopteryx signata	17,500	21	10
Pteronarcella badia	42,500	7	0
Pteronarcella badia	18,000	4	50
Pteronarcys californica	14,000	14	100
Tricoptera			
Tricopteran larva (Leptoceridae)	2,000	4	50
Brachycentrus americanus	42,500	7	100
Zygopteran nymph	250	4	50
Daphnia magna	100	(1)	50
(in Lake Superior water)	650	(1)	50

(Clubb et al., 1975)

(1) Time not specified

chloride, were manifested in kidney intestine, gill, epidermis, and hemopoietic tissue (Newman and MacLean, 1974).

Invertebrates

Earthworms appear to be able to concentrate cadmium. Crickets, feeding on ^{109}Cd-labeled vegetation rapidly accumulated cadmium but not above the level of concentration of the food source. Spiders feeding on these crickets accumulated and excreted cadmium slowly but, similarly, did not concentrate it above the level in the food source (Fassett, 1975). Pink shrimp were exposed for 30 days to varying concentrations of cadmium. Accumulation is summarized in Table 15.

TABLE 15. Cadmium accumulation by pink shrimp

Cd (mg/l)	Concentration Factor
-----	--
0.079	48
0.162	57
0.307	55
0.586	53
0.866	54
1.265	23

(25 C, salinity 20 o/oo)

(Nimmo et al., 1977)

After 96 h exposure of pink shrimp (Pinaeus duorarum) to cadmium (as $CdCl_2$), it was found that the tissue concentration was proportional to water concentration with concentration factors of 25 to 57 and cadmium concentrations differed by 5 orders of magnitude among tissues analyzed: hepatopancreas > exoskeleton > muscle > serum. The shrimp were then placed in cadmium-free flowing seawater and held for 7 days. Only in the muscle and serum were changes noted: a significant decrease in the serum and a significant increase in muscle. Pink shrimp excreted about 50% of the cadmium in 7-10 days (Nimmo et al., 1977). In other studies, Meganyctiphanes norvigica excreted 97% after 96 days (Benayoun et al., 1974).

Acute and subacute exposure of pink shrimp to cadmium produced blackened foci or melanized lamellae. In acute exposure, shrimp exposed to cadmium developed "black gills" (Nimmo et al., 1977).

When pink shrimp (Penaeus duorarum) was exposed to cadmium (765 µg/l) for 15 days, the gills became necrotic. Local and extensive areas of cell death were observed in the distal gill filaments. Such destruction of cells could cause osmoregulatory, respiratory and detoxifying dysfunctions (Couch, 1977).

Pink Shrimp and grass shrimp (P. vulgaris) bioaccumulated cadmium from water even at concentrations. Gill lamellae of P. vulgaris were also blackened, necrotic and distended due to congestion with large numbers of hemocytes after exposure to 75 µg Cd/l for 10 days. Brine shrimp (Artemia) containing cadmium were used as food for grass shrimp. Bioaccumulation was poor and the transfer of cadmium from brine shrimp to grass shrimp was much lower than from the water (Nimmo et al., 1977).

Pink shrimp were exposed to cadmium, methoxychlor and PCBs, singly and in combination. Methoxychlor influenced the accumulation and loss of cadmium from shrimp. Less cadmium was found in the muscle of shrimp exposed to the combination than in the absence of methoxychlor (Table 16) (Nimmo and Bahner, 1976).

TABLE 16. Accumulation of cadmium in shrimp exposed to multiple compounds[1]

Exposure Level	PCB[2] (μg/l)	Methoxychlor (μg/l)	Concentration Factor
640	---	---	24
774	---	1.1	13
746	0.9	---	19
829	0.9	0.8	20

(Nimmo and Bahner, 1976)

[1] 10-day flowing water bioassays; 20 o/oo, 25 C

[2] Aroclor 1254

Marine and estuarine species of isopods (Crustacea) were exposed to varying salinity and temperature in the presence and absence of cadmium ($3CdSO_4 8H_2O$). In 100% sea water, mortality was low in the presence of 10 and 20 ppm cadmium. When the salinity was decreased, mortality increased. Temperature increases also increased toxicity of cadmium (Table 17). In *Jaera albifrons sensu stricto*, cadmium also altered osmoregulatory ability (Jones, 1975).

TABLE 17. Lethal time of cadmium x salinity to isopods

		LT_{50}		
Species	Cd concn. (ppm)	time (h)	sea water (%)	Temp. (^{0}C)
Idotea baltica	10	120	100	
		34	40	
	20	67	100	
		56	80	
		38	60	
		<24	40	
Idotea neglecta	10	95	100	5
		86	80	
		64	60	
		26	40	
	10	108	100	10
		61	80	
		52	60	
		26	40	
Jaera albifrons sensu stricto	10	>120	100	5
		46	1	
	10	>120	100	10
		29	1	

After eating food containing 13-15 μg/g, people have become ill. Because seafood constitute a source of cadmium in the human diet and the known ability of shellfish to accumulate trace metals, American oyster (Crassostrea virginica) was exposed to 0.005 ppm cadmium. Within 40 weeks, the cadmium concentration in oyster tissues had increased from a background of about 3 μg/g to more than 13 μg/g (dry wt). This level could pose a potential health hazard when oysters constitute a major diet item (Zaroogian and Cheer, 1976). At 0.010 ppm cadmium in flowing sea water, residues in American oysters quickly exceeded 13 μg/g; at 0.025 ppm and 0.100 ppm, this level was surpassed in 5 and 2 weeks, respectively (Shuster and Pringle, 1969). Analyses of the Pacific oyster (Crassostrea gigas) from the Tamar River, Tasmania, showed cadmium residue levels of 63 ppm. Oysters from one site have caused vomiting but no cases of cadmium poisoning were diagnosed (Thrower and Eustace, 1973a, b; Ratkowsky et al., 1974). The Pacific oyster accumulated cadmium to 25 ppm from a level of about 1 ppm in the mud of their bed (Ayling, 1974).

Cadmium exposed oysters Crassostrea virginica exhibited very little shell growth, emaciation, loss of pigmentation of the mantle edge, and coloration of the digestive diverticulae. At the levels studied, 0.1 and 0.2 ppm, mortality was 84% (126/150) and 100% (150/150), respectively. Residue levels exceeded 100 ppm at both exposure levels before 20 weeks exposure (Shuster and Pringle, 1969). At 3.8 ppm cadmium was toxic to 50 % of exposed oyster embryos with 48 h (26C) (Table 18) (Calabrese et al., 1973).

TABLE 18. Heavy metal toxicity to oyster embryos

(48 h at 26C ± 1 C)

Salt	LC_{50}(ppm)
Mercuric chloride	0.0056
Silver nitrate	0.0058
Cupric chloride	0.103
Zinc chloride	0.31
Nickel chloride	1.18
Lead nitrate	2.45
→ Cadmium chloride	3.80
Sodium arsenite	7.50
Chromium chloride	10.3
Manganese chloride	16.0

Crabs are capable of autotomizing injured appendages and regenerating them. When fiddler crabs (_Uca pugilator_) were exposed to 0.1 mg/l of cadmium, some retarding of regeneration occurred (Weis, 1976).

When exposed to cadmium, accumulation by fiddler crabs was maximal at high termperature and low salinity (O'Hara, 1973a). In other studies, the lethality of cadmium to fiddler crabs was found to be salinity and temperature dependent (Table 19). Lethality also was greatest at high temperature and low salinity (O'Hara, 1973b).

TABLE 19. Cadmium toxicity to fiddler crabs

			TL$_m$
Temperature, C	Time, h	Salinity, o/oo	Cd, ppm
10	144	10	51.0
	192		28.5
	240		15.7
	192	20	52.0
	240		42.0
	240		47.0
20	96	10	32.2
	144		21.3
	192		18.0
	240		11.8
	96	20	46.6
	144		23.0
	192		16.5
	240		9.5
	96	30	37.0
	144		29.6
	192		21.0
	240		17.9
30	48	10	11.0
	96		6.8
	144		4.0
	192		3.0
	240		2.9
	48	20	28.0
	96		10.1
	144		5.2
	192		3.7
	240		3.5
	48	30	33.3
	96		23.3
	144		7.6
	192		6.5
	240		5.7

Mature and immature snails (Physa gyrina) were exposed to Cd^{+2}. The LC$_{50}$ was 1.37 ppm and 0.43 ppm, respectively. The rate of uptake, 0.550 ppm/h, was twice the rate of depuration, 0.229 ppm/h. This allowed accumulation of Cd^{+2} in the snail (Wier and Walter, 1976).

Bay scallops exposed to levels of Cd^{++} ranging from 0.75 ppm to 2.0 ppm accumulated up to about 60 ppm of cadmium (Nelson et al., 1976).

TABLE 20. Cadmium uptake by scallops

Exposure level (ppm)	Uptake (ppm)	Biomagnification factor
0.75	49.4 ± 4.1	
1.0	54.1 ± 2.2	54
1.25	55.8 ± 1.9	44
1.5	58.9 ± 1.9	39
1.75	57.4 ± 4.0	32
2.0	60.8 ± 5.1	30

Zooplankton is the main source of food for some species of fish and destruction of this fish food source could result in the disappearance of some fish. Three representative species of freshwater zooplankton were collected and exposed to cadmium. The 48 h-LC_{50} was determined for the three species and is summarized in Table 21 (Baudouin and Scoppa, 1974).

TABLE 21. Toxicity of cadmium to aquatic organisms

	48 h-LC_{50} (μg/l)
Cyclops abyssorum	3,800
Eudiaptomus padanus	550
Daphnia hyalina	55

Daphnia magna were exposed to Cd^{+2}. At 0.17 μg/l there was a 16% reproductive impairment after 3 weeks. In Lake Superior water, the LC_{50} was 65 μg/l in the absence of food. The chronic (3-week) LC_{50} was 5 μg/l with a range of 4.0-6.2. A 50% reproductive impairment occurred at 0.7 μg/l (Biesinger and Christensen, 1972). The threshold concentration of cadmium chloride on Lake Erie water for immobilization of Daphnia magna was found to be less than 2.6 ppb (Anderson, 1948).

Exposure of adult Artemia salina (L.) and Ophryotrocha labronica (LaGreca and Bacci) to 1.0 ppm $CdSO_4$ resulted in 50% mortality in 240 and 410 h, respectively (Brown and Ahsanullah, 1971).

Aquatic Plants

Concentrations of cadmium as low as 6.1 ppb significantly inhibited growth of the alga Scenedesmus quadracauda; 61 ppb and higher severely inhibited growth (Klass et al., 1974).

The southern naiad (Najas quadulepensis), a pond weed, was exposed to cadmium. Toxic reactions and accumulation of cadmium increased as exposure levels increased. At an exposure level of 0.83 mg/l, cadmium accumulation exceeded 5000 μg/g ash. Studies with this aquatic plant indicated that there was a potential for introduction of potentially toxic quantities of cadmium into the food chain of higher organisms such as sunfish and waterfowl (Cearley and Coleman, 1973).

Terrestrial Plants

Plant cadmium is influenced by a complexity of interrelationships of elements within plants. Direct and indirect influence may be influenced by availability of nutrients and other elements. Tissue concentration, uptake and translocation of cadmium to the tops of hydroponically-grown oats and lettuce was reduced by increasing K supply or pH of the solution. Addition of Ca, Zn, or Al reduced cadmium in a specific tissue or crop (John, 1976). Some evidence indicated that cadmium uptake and translocation are genetically controlled (John and van Laerhoven, 1976).

Summary

Cadmium is ubiquitous and finds its way into the environment from pesticides containing cadmium, from mine drainage, from burning fossil fuels, and from cadmium plating and other industrial effluents. Effects on mammals, birds, fish and invertebrates have been observed. In mammals, studies have shown that cadmium ingestion may cause hypertension and adversely affect syntheses of steroid hormones. As in humans, heaviest deposition occurs in kidney and liver. Inhibition of vasopressor responses were also observed. In birds, kidney and testicular necrosis was observed. Chronic exposure also produced severe anemia and some growth retardation.

A study of cadmium in a stream ecosystem showed distribution throughout all components. Residues in fish and sediment were similar but higher than in the water. Highest concentrations were found in aquatic insects (Table 21) (Enk and Mathis, 1977).

Chronic exposure at 10 ppm cadmium caused egg production of zebra fish to decline; increasing salinity, in the presence of cadmium, adversely affected herring reproduction; and exposure of fathead minnow embryos to less than 1 ppm cadmium decreased survival. Increased terata were observed in bluegill fish at less than 1 ppm. Goldfish tissue and plasma exhibited deviations in levels of sodium and chloride. Testicular necrosis and altered steroid syntheses were observed in brook trout. Bioconcentration was also observed in fish.

Shrimp and other invertebrates were also adversely affected by cadmium exposure. Shrimp gills became necrotic. Mortality in all species was dose related. Decreased salinity, at a constant cadmium exposure level, caused increased shrimp mortality. Oysters were shown to be capable of concentrating cadmium to a level that could pose a potential health hazard. At an exposure level of 1 ppm, oyster mortality was 84%. At 3.8 ppm, 50% of exposed oyster embryos died within 48 hours. At 0.1 ppm, retardation of regeneration by fiddler crabs occurred.

Bioaccumulation of cadmium seems almost universal in the aquatic environment. Studies with a pond weed, the southern naiad, showed that it was capable of accumulating cadmium and that here was an avenue to introduce potentially toxic amounts of cadmium into the food chain of higher organisms.

TABLE 21. Cadmium distribution in a stream

Source		Range, ppm
Mayflies	(*Isonychia* sp.)	0.79 - 1.71
Damselflies	(*Agrion* sp.)	1.00 - 1.98
Caddisflies	(*Cheumatopsyche* sp.)	0.73 - 0.99
	(*Hydropsyche* sp.)	0.22 - 0.85
River carpsucker		0.06 - 0.09
Fantail darter		0.08 - 0.32
Smallmouth bass		0.05 - 0.19
Sediment		0.08 - 0.23
Water		<0.02

BIBLIOGRAPHY

Anderson, B.G.
1948. The Apparent Thresholds of Toxicity to *Daphnia Magna* for Chlorides of Various Metals when added to Lake Erie Water. Trans. Am. Fish. Soc., 78:96-113.

Anderson, S.H., A.W. Andren, C.F. Baes, III, G.J. Dodson, W.F. Harris, G.S. Henderson, D.E. Reichle, J.D. Story, R.I. Van Hook, W. Van Winkle, and A. J. Yates.
1974. Ecology and Analysis of Trace Contaminants. Environmental Monitoring of Toxic Materials in Ecosystems. ORNL- NSF-EATC-6, 95-120.

Aston, S.R., R. Chester, A. Griffiths and J.P. Riley
1972. Distribution of cadmium in North Atlantic deep-sea sediments. Nature 239:393

Axelsson, Bengt and M. Piscator.
1966a. Renal Damage After Prolonged Exposure to Cadmium. Arch. Environ. Health, 12:360-373.

Axelsson, B. and M. Piscator.
1966b. Serum Proteins in Cadmium Poisoned Rabbits. Arch. Environ. Health, 12:374-381.

Axelsson, B., S.E. Dahlgren, and M. Piscator.
1968. Renal Lesions in the Rabbits After Long-Term Exposure to Cadmium. Arch. Environ. Health, 17:24-28.

Ayling, G.M.
1974. Uptake Of Cadmium, Zinc, Copper, Lead and Chromium in the Pacific Oyster, Crassostrea Gigas, Grown in the Tamar River, Tasmania. Water Res., 8:729-738.

Bahner, L.H., and D.R. Nimmo
1975. Methods to assess effects of combinations of toxicants, salinity, and temperature on estuarine animals. pp. 169-177. In: Trace Substances in Environmental Health - IX. University of Missouri at Columbia.

Ball, I.R.
1967. The Toxicity of Cadmium to Rainbow Trout (*Salmo Gairdnerii* Richardson). Water Res., 1:805-806

Baudouin, M.F. and P. Scoppa.
1974. Acute Toxicity of Various Metals to Freshwater Zooplankton. Bull. Environ. Contam. Toxicol., 12(6):745-751.

Benayoun, G., S.W. Fowler, and B. Oregioni
1974. Flux of cadmium through euphausiids. Mar. Biol., 27:205-212.

Benoit, D.A., E.N. Leonard, G.M. Christensen, and J.T. Fiandt.
1976. Toxic Effects of Cadmium on Three Generations of Brook Trout (*Salvelinus fontinalis*). Trans. Am. Fish. Soc., 105(4):550-560.

Biesinger, K.E. and G.M. Christensen.
1972. Effects of Various Metals on Survival, Growth, Reproduction, and Metabolism of *Daphnia magna*. J. Fish. Res. Bd. Can., 29(12):1691-1700.

Blaylock, B.G., R.A. Goldstein, J.W. Huckabee, S. Janzen, C. Matti, R.O. Olmstead, M. Slawsky, R.A. Stella, and J.P. Witherspoon.
1973. Ecology and Analysis of Trace Contaminants. Ecology of Toxic Metals. ORNL-NSF-EATC-1, 121-160.

Bondietti, E.A., R.M. Perhac, F.H. Sweeton, and T. Tamura.
1973. Ecology and Analysis of Trace Contaminants. Toxic Metals in Lake and River Sediments. ORNL-NSF-EATC-1, 166-213.

Brown, B. and M. Ahsanullah.
1971. Effect of Heavy Metals on Mortality and Growth. Mar. Pollut. Bull., 2(12):182-187.

Calabrese, A., R.S. Collier, D.A. Nelson, and J.R. MacInnes.
1973. The Toxicity of Heavy Metals to Embryos of the American Oyster *Crassostrea virginica*. Mar. Biol., 18:162-166.

Cearley, J.E., and R.L. Coleman.
1973. Cadmium Toxicity and Accumulation in Southern Naiad. Bull. Environ. Contam. Toxicol., 9(2):100-101.

Cearley, J.E., and R.L. Coleman.
1974. Cadmium Toxicity and Bioconcentration in Largemouth Bass and Bluegill. Bull. Environ. Contam. Toxicol., 11(2):146-151.

Clubb, R.W., A.R. Gaufin, and J.L. Lords.
1975. Acute Cadmium Toxicity Studies Upon Nine Species of Aquatic Insects. Environ. Res., 9:332-341.

Collier, R.S., J.E. Miller, M.A. Dawson, and F.P. Thurberg.
1973. Physiological Response of the Mud Crab, *Eurypanopeus depressus* to Cadmium. Bull. Environ. Contam. Toxicol., 10(6):378-382.

Couch, J.A.
1977. Ultrastructural Study of Lesion in Gills of a Marine Shrimp Exposed to Cadmium. J. Invert. Pathol., 29:267-288.

Eaton, J.G.
1974. Chronic Cadmium Toxicity to the Bluegill (*Lepomis macrochirus Rafinesque*). Trans. Am. Fish. Soc., 103(4)729-735.

Eisler, R.
1971. Cadmium Poisoning in *Fundulus heteroclitus* (Pisces: *Cyprinodontidae*) and other Marine Organisms. J. Fish. Res. Bd. Can., 28:1225-1234.

Eisler, R. and G.R. Gardner.
1973. Acute Toxicology to an Estuarine Teleost of Mixtures of Cadmium, Copper and Zinc Salts. J. Fish. Biol., 5:131-142.

Enk, M.D. and B.J. Mathis
1977. Distribution of cadmium and lead in a stream ecosystem. Hydrobiol., 53(2-3):153-158.

Fassett, D.W.
1975. Cadmium: Biological Effects and Occurrence in the Environment. Ann. Rev. Pharmacol., 15:425-435.

Fischer, G.M. and G.S. Thind
1971. Tissue Cadmium and Water Content of Normal and Cadmium Hypertensive Rabbits. Arch. Environ. Health, 23:107-110.

Fleischer, M., A.F. Sarofim, D.W. Fassett, P. Hammong, H.T. Shacklette, I.C.T. Nisbet and S. Epstein
1974. Environmental impact of cadmium. Environ. Hlth. Perspect., 7:253-323.

Fox, M.R.S and B.E. Fry, Jr.
1970. Cadmium Toxicity Decreased by Dietary Ascorbic Supplements. Science, 169:989-991.

Freeman, H.C. and G.B. Sangalang
1977. A study of the effects of methyl mercury, cadmium, arsenic, selenium, and a PCB, (Aroclor 1254) on adrenal in testicular steroidogeneses *in vitro*, by the Gray Seal *Halichoerus grypus*. Arch. Environ. Contam. Toxicol., 5:369-383.

Gardner, G.R. and P.P. Yevich
1969. Toxicological Effects of Cadmium on *Fundulus heteroclitus* Under Various Oxygen, pH, Salinity and Temperature Regimes. Amer. Zool., 9(4):1096.

Gardner, G.R. and P.P. Yevich
1970. Histological and Hematological Responses of an Estuarine Teleost to Cadmium. J. Fish. Res. Bd. Can., 27:2185-2196.

Greig, R.A., D.R. Wenzloff, and J.B. Pearce
1976. Distribution and Abundance of Heavy Metals in Finfish, Invertebrates and Sediments Collected at a Deepwater Disposal Site. Mar. Pollut. Bull., 7(10):185-187.

Horvath, G.J., R.C. Harriss, and H.C. Mattraw
1972. Land Development and Heavy Metal Distribution in the Florida Everglades. Mar. Pollut. Bull., 3(12):182-184.

John, M.K.
1976. Interrelationships Between Plant Cadmium and Uptake of Some Other Elements from Culture Solutions by Oats and Lettuce. Environ. Pollut., 11:85-95.

John, M.K. and C.J. van Laerhoven
1976. Differential Effects of Cadmium on Lettuce Varieties. Environ. Pollut., 10:163-173.

Jones, J.R.E.
1939. The Relation Between the Electrolytic Solution Pressures of the Metals and their Toxicity to the Stickleback (*Gasterosteus Aculeatus L.*) J. Exptl. Biol., 16:425-437.

Jones, M.B.
1975. Synergistic Effects of Salinity, Temperature and Heavy Metals on Mortality and Osmoregulation in Marine and Estuarine Isopods (*Crustacea*). Mar. Biol., 30:13-20.

Klass, E., D.W. Rowe, and E.J. Massaro
1974. The Effect of Cadmium on Population Growth of the Green Alga *Scenedesmus quadracauda*. Bull. Environ. Contam. Toxicol., 12(4):442-445.

Kumada, H., S, Kimura, M. Yokote, and Y. Matida
1973. Acute and Chronic Toxicity, Uptake and Retention of Cadmium in Freshwater Organisms. Bull. Freshwater Fish. Res. Lab. Tokyo, 22(2):157-165.

Lucas, H.F. Jr., D.N. Edgington, and P.J. Colby
1970. Concentrations of Trace Elements in Great Lakes Fishes. J. Fish. Res. Bd. Can., 27:677-684.

McCarty, L.S. and A.H. Houston
1976. Effects of exposure to sublethal levels of cadmium upon water-electrolyte status in the goldfish (Carassius auratus). J. Fish. Biol., 9:11-19.

Negilski, D.S.
1976. Acute Toxicity of Zinc, Cadmium and Chromium to the Marine Fishes, Yellow-eye Mullet (*Aldrichetta forsteri* C.& V.) and Small-mouthed Hardyhead (*Atherinasoma microstoma* Whitley). Aust. J. Mar. Freshwater Res., 27:137-149.

Nelson, D.A., A. Calabrese, B.A. Nelson, J.R. MacInnes, and D.R. Wenzloff
1976. Biological Effects of Heavy Metals on Juvenile Bay Scallops, *Argopecten irradians*, in Short-term Exposures. Bull. Environ. Contam. Toxicol., 16(3):275-282.

Newman, M.W. and S.A. MacLean
1974. Physiological response of the cunner, *Tautogolabrus adspersus*, to cadmium. VI. Histopathology. NOAA Tech Report NMFS SSRF, 681:27-33.

Nickless, G. R. Stenner, and N. Terrille
1972. Distribution of Cadmium, Lead and Zinc in the Bristol Channel. Mar. Pollut. Bull., 3(12):188-190.

Nimmo, D.W.R. and L.H. Bahner
1976. Metals, Pesticides and PCBs: Toxicities to Shrimp Singly. Estuarine Processes, Vol. I, Uses, Stresses, and Adaption to the Estuary, Academic Press, Inc., p. 523-532.

Nimmo, D.W.R., D.V. Lightner, and L.H. Bahner
1977. Effects of Cadmium on the Shrimps, *Penaeus duorarum*, *Palaemontes pugio* and *Palaemonetes vulgaris*. Physiological Responses Of Marine Biota To Pollutants, Academic Press Inc., p. 131-183.

Nimmo, D.W.R., R.A. Rigby, L.H. Bahner, and J.M. Sheppard
In Press. The Acute and Chronic Effects of Cadmium on the Estuarine Mysid, *Mysidopsis bahia*. Bull. Environ. Contam. Toxicol.

O'Hara, J.
1973a. Cadmium Uptake by Fiddler Crabs Exposed to Temperature and Salinity Stress. J. Fish. Res. Bd. Can., 30:846-848.

O'Hara, J.
1973b. The Influence of Temperature and Salinity on the Toxicity of Cadmium to the Fiddler Crab, *Uca Pugilator*. Fish. Bull., 71(1): 149-153.

Peden, J.D., J.H. Crothers, C.E. Waterfall, and J. Beasley
1973. Heavy Metals in Somerset Marine Organisms. Mar. Pollut. Bull., 4(1):7-9.

Pickering, Q.H. and M.H. Gast
1972. Acute and chronic toxicity of cadmium to the fathead minnow (*Pimephales promelas*). J. Fish. Res. Bd. Can., 29: 1099-1106.

Piscator, M. and B. Axelsson
1970. Serum Proteins and Kidney Function After Exposure to Cadmium. Arch. Environ. Health, 21:604-608.

Ratkowsky, D.A., S.J. Thrower, I.J. Eustace, and J. Olley
1974. A Numerical Study of the Concentration of Some Heavy Metals in Tasmanian Oysters. J. Fish. Res. Bd. Can., 31:1165-1171.

Rehwoldt, R., D. Karimian-Teherani
1976. Uptake and Effect of Cadmium on Zebrafish. Bull. Environ. Contam. Toxicol., 15(4):442-445.

Riley, J.P. and D.A. Segar
1970. The Distribution of the Major and Some Minor Elements in Marine Animals. J. Mar. Biol. Ass. U.K., 50:721-730.

Rowe, D.W. and E.J. Massaro
1974. Cadmium Uptake and Time Dependent Alterations in Tissue Levels in the White Catfish *Ictalurus catus* (Pisces: *Ictaluridae*). Bull. Environ. Contam. Toxicol., 11(3)244-249.

Sangalang, G.B. and M.J. O'Halloran
1972. Cadmium-induced Testicular Injury and Alterations of Androgen Synthesis in Brook Trout. Nature, 240:470-471.

Shuster, C.N.,Jr. and B.H. Pringle
1969. Trace Metal Accumulation by the American Eastern Oyster. *Crassostrea Virginica*. Proc. Nat. Shellfish Assoc., 59:91-103.

Smith, B.P., E. Hejtmancik, and B.J. Camp
1976. Acute Effects of Cadmium on *Ictalurus punctatyus* (Catfish). Bull. Environ. Contam. Toxicol., 15(3)271-277.

Thind, G.S., K.F. Stephan, and W.S. Blakemore
1970. Inhibition of Vasopressor Response by Cadmium. Am. J. Physiol., 219(3):577-583.

Thorp, V.J. and P.S. Lake
1974. Toxicity Bioassays of Cadmium on Selected Freshwater Invertebrates and the Interaction of Cadmium and Zinc on the Freshwater Shrimp, *Paratya tasmanienis* Riek. Aust. J. Mar. Freshwater Res., 25:97-104.

Thrower, S.J., and I.J. Eustace
1973a. Heavy metals in Tasmanian oysters in 1972. Aust. Fish., 32(10):7-10.

Thrower, S.J., and I.J. Eustace
1973b. Heavy metal accumulation in oysters grown in Tasmanian waters. Food Technol. Aust., 25:546-553.

Thurberg, F.P. and M.A. Dawson
1974. Physiological response of the cunner, Tautogolabrus aaspersus, to cadmium. III. Changes in osmoregulation and oxygen consumption. NOAA Tech. Report NMFS SSRF, 681:11-13.

Uthe, J.F. and E.G. Bligh
1971. Preliminary Survey of Heavy Metal Contamination of Canadian Freshwater Fish. J. Fish. Res. Bd. Can., 28:786-788.

von Westernhagen, H., H. Rosenthan, and K.-R. Sperling
1974. Combined effects of cadmium and salinity on development and survival of herring eggs. Helgolander wiss. Meeresunters, 26:416-433.

Weis, J.S.
1976. Effects of Mercury, Cadmium, and Lead Salts on Regeneration and Ecdysis in the Fiddler Crab, Uca Pugilator. Fish. Bull., 7(2):464-466.

White, D.H., M.T. Finley, and J.F. Ferrell
In Press. Histopathological Effects of Dietary Cadmium on Kidneys and Testes of Mallard Ducks. J. Toxicol. Environ. Health,

Wier, C.F. and W.M. Walter
1976. Toxicity of Cadmium in the Freshwater Snail, Physa gyrina Say. J. Environ. Qual., 5(4):359-362.

Wright, D.A.
1976. Heavy Metals in Animals from the North East Coast. Mar. Pollut. Bull., 7(2):36-38.

Zaroogian, G.E. and S. Cheer
1976. Accumulation of Cadmium by the American oyster, Crassostrea virginica. Nature, 261:408-409.

EFFECTS OF CADMIUM ON FISH AND WILDLIFE

MR. JORCZYK: Ed Jorczyk, 3M Company. Most of the cadmium that enters the environment from plating operations probably is in the form of cadmium cyanide. I imagine your studies didn't use cadmium cyanide as such. Which would be more toxic, cadmium or cyanide?

MR. MENZIE: I would suspect that cyanide would be quite toxic to the mammals. It operates at a low, basic level and ties up many enzymes.

Cyanide compounds have not been used to test the toxicity of cadmium in order to eliminate as many of the variables as possible. The toxicity of the different cadmium salts, chloride, acetate and so forth, are approximately the same, and so these are the ones that are used in such studies.

MR. WHITE: Marty White, Cadmium Association. Can you comment on the relative toxicity to freshwater and marine fish of cadmium compared with zinc, copper, nickel and chromium? I believe zinc is also highly toxic to these particular fish.

Our main interest is the way that cadmium can get into the food chain. What about the off-shore fish, the major foods? Compared with cadmium levels in the ocean, do these food fish accumulate cadmium? What levels of cadmium do you find on your fishmongers' slab?

MR. MENZIE: I am not sure I can remember all the parts of the question, but I will try. The first slide projections that I showed indicated differences in accumulation in some commercial species of fish. Young cod were examined with somewhat different levels in different tissues. The levels of cadmium seem to be more related to the proximity to industrial areas, higher levels being reflected in areas close in shore.

Samples collected in the vicinity of a deepwater dump site in the middle Atlantic bite when compared to samples taken from the dump site in the New York bite indicate that the muscle levels were quite low, being in the order of a tenth of a part per million on a wet-weight basis, from the deepwater area. A series of samples from the dump site in the New York bite were found to contain over one part per million. If you will repeat your other questions, I will be glad to answer them.

MR. WHITE: Everyone agrees that cadmium is toxic to fish. I am trying to get an idea of the toxicity of the other plating chemicals such as zinc, chromium and nickel.

MR. MENZIE: All right. In one of the overhead slides, I had a comparison of the toxicity of a number of salts to oyster embryos. If I can refer to that, in the order, mercury, silver, copper, zinc, nickel, lead, cadmium, sodium arsenite, and chromium chloride. Chromium chloride is about three times as toxic as chromium, and about four times as toxic as manganese.

These are chlorides, copper being quite toxic, on the order of about 30 times as toxic as cadmium; zinc being about an order of 10; nickel about three times as toxic.

MR. WHITE: So basically, we have got a problem with all the metal finishing metals, not just cadmium.

MR. MENZIE: Heavy metals in general are a problem for aquatic organisms.

MR. GROBIN: Allen Grobin, IBM Corporation. Is pollution from electroplating the most serious cause of the problem for the aquatic life? Or is it the corrosion of the plated metals in place? Which of these things plays the greatest role? Is there any differentiation at all?

MR. MENZIE: I haven't differentiated. I am not sure to what extent I can differentiate the sources. We have a general idea where cadmium is coming from. Some publications report that the biggest single source of cadmium in the environment is probably industrial, and that includes electroplating.

I am not in a position to quantify this. I really don't know which is the major source of pollution. Certainly the effluents that come from industrial sources play a tremendous part.

MR. GROBIN: I think one of the comments this morning made by one of the gentlemen from the Air Force was that when they wash their planes, aren't they indeed putting cadmium into the environment?

MR. MENZIE: There are a number of non-point sources, but the relationship between cadmium residue levels and proximity to industrialized areas implicates industry as being the major contributor.

Alternative Materials and Processes

Session IV

Wednesday Afternoon 2:20

A NEW NON-CYANIDE ELECTROPLATING BATH

Edward R. Jorczyk
3M Company
Plating Systems Department
Saint Paul, Minnesota 55101

Cadmium metal has been electroplated almost exclusively from a cyanide type solution for a least 45 years. Development on other systems lagged because overall characteristics of the cyanide bath could not be improved upon. The enactment of laws prohibiting the discharge of cadmium and cyanide containing wastes into waterways and sewer systems prompted new investigations. An acid sulfate cadmium bath has been developed which plates a bright deposit equivalent to that obtained from a cyanide bath. It is easily controlled. The metal content is kept within limits by the use of both cadmium and insoluble carbon anodes. The metal content is 2 oz./gal., compared to 2.6 to 4.5 oz./gal. for cyanide baths. Therefore, less metal is dragged out into the waste water effluent. The acid sulfate cadmium bath eliminates the use of toxic sodium cyanide, which ranges in concentrations from 10 to 21 oz./gal., depending upon the type of parts being plated. Savings are realized since cyanide waste treatment costs are eliminated. Cadmium concentration parameters in the discharge effluent are readily attained by raising the pH of the acid sulfate cadmium solution or effluent to a pH of 10.5 and removing the precipitated cadmium hydroxide by conventional means.

Preceding page blank

A NEW NON CYANIDE CADMIUM ELECTROPLATING BATH

Edward R. Jorczyk
3M Company
3M Center
St. Paul, Mn. 55101

Cadmium has been plated commercially from the cyanide bath for at least fifty years. Over the years, considerable work has been done to optimize bath compositions. Today's organic additives are exceptionally stable. Cadmium deposits are uniform, fine grained, and bright. The bath has a wide current density plating range, good throwing power and is easy to control.

There are various cadmium cyanide plating bath compositions[1] that may be used depending on whether parts are plated in a barrel or on a rack and whether a high throw formulation is required. Other variables also have to be considered. Most baths will fall into composition ranges as given in Table I.

When one considers the environment, cadmium cyanide plating solutions present a twofold problem. Both cadmium and cyanide are very toxic substances. Before plating effluent containing cadmium and cyanide can be discharged, it must be treated to reduce these substances to a concentration level that meets local requirements as well as EPA guidelines.

It was apparent in the late 1960's that toxic substances should not be discharged into the environment if their concentrations were above those specified by regulatory agencies. It was also apparent, as has happened, that stricter discharge limits could be anticipated, with talk of zero discharge on some chemicals.

During recent years, there were crash programs by suppliers of proprietary plating and chemical products to develop new products that contained non polluting chemicals and that were easily treated in order to remove undersirable constituents prior to their discharge to the environment.

One of the first major changes that came about in the electroplating field was bright zinc plating from other than cyanide type baths. In 1967 a neutral zinc chloride bath[2] containing no cyanide was introduced. Today, after a few years, there have evolved non cyanide alkaline baths, ammonium chloride[3] and potassium chloride baths which have replaced many cyanide type baths.

The development of non cyanide cadmium plating baths has not kept pace with the changes that took place in zinc plating baths. The reasons are obvious. The total zinc gallonage is estimated to be ten to twenty times that of cadmium. Also the possibility of limitations and restrictions on the use of cadmium plate resulted in a wait and see attitude. Therefore most research dollars were channeled into zinc plating rather than cadmium plating.

The new non cyanide cadmium bath can be termed an acid sulfate bath. In the past, other acid baths have been introduced, but deposits were not bright or fine grained. Control was also difficult. This new bath plates deposits which are bright and fine grained. The deposit may be clear or iridescent chromated to impart further corrosion protection.

The bath is suitable for both rack and barrel plating. Throwing power is considered adequate. A high throw formulation is available for parts with deep recesses.

Substrates such as steel, copper, brass, malleable and cast iron, and carbo-nitrided surfaces usually plated in the cyanide bath may also be plated in the acid sulfate bath. In addition, stainless steel can also be plated in the acid sulfate bath without using a nickel strike. The bath make up is given in Table II. The solution has a composition as follows:

Cadmium metal 15 g/l (2.0 oz./gal.)

Free Sulfuric Acid, Sp.Gr. 1.84 23.4 ml/l (3.0 fl.oz./gal.).

The bath has a fairly wide operating range as given in Table III.

Advantages and Disadvantages

Acid resistant equipment is required. Since the alkaline cadmium cyanide baths may be contained in bare steel, there is some reluctance to change because a monetary expenditure is required for either equipment modification or new equipment. However, when faced with a capital expenditure for cyanide treatment equipment and continuing cost of treatment chemicals, the alternative to change to the acid sulfate bath becomes more attractive. The plater who has no cyanide type baths in his plant may now add the acid sulfate cadmium bath.

When platers switched from cyanide zinc to the chloride zincs, more thorough cleaning procedures were commonly adopted. The same procedures should be used with the acid sulfate bath.

Chromating solutions used for deposits plated from alkaline or cyanide baths are not always suitable for acid sulfate deposits, and special chromating solutions are available.

Cathode efficiency of the acid sulfate bath is less than the cyanide baths; however, a bath composition utilizing both sulfuric and fluoboric acid results in efficiencies slightly higher than those found in cyanide baths. The sulfate-fluoborate bath will not be covered in this paper.

Since cyanide, ammonium ions, chelating, or complexing agents are not present in the bath, waste treatment is simple and economical.

Less cadmium is dragged out resulting in potential savings.

No carbonate is formed as in the cyanide bath; therefore no down time for its removal is required.

Equipment

Equipment requirements are listed in Table IV.

Anodes

Carbon anodes are used in conjunction with slab cadmium anodes because cathode efficiency is less than 100%, which means some of the current that would be used to deposit metal is used to deposit hydrogen. Cathode efficiencies can vary from nearly 100% at 5 A.S.F. to 70% at 20 A.S.F.

Since the cadmium anode efficiency is nearly 100%, the metal content of the bath would continue to increase to a point where the metal concentration is above the recommended range.

To offset this, a ratio of approximately 2 carbon anodes to 1 cadmium anode is used. Some trial and error may initially be required to balance the amount of cadmium plated out and lost by drag out to that put back into the solution from anodes.

Analysis and Control

Cadmium and sulfuric acid content are determined by simple analytical procedures. CADVERT No. 375 is added at the rate of 120 to 240 ml (4 to 8 fl.oz.) per 1000 ampere hours of operation. CADVERT No. 374 is added to replace loss by drag-out at the rate of 10% by volume of the amount of sulfuric acid added.

Further control may be had using a Hull cell test.

Waste Treatment

The cadmium metal may be precipitated from the rinse water by raising the pH to 10.5 with either sodium hydroxide or hydrated lime. The precipitated cadmium may be removed by filtration, settling or decantation. The filtrate should have a cadmium concentration of less than 0.5 ppm.

REFERENCES

1. 45th Guidebook Directory for Metal Finishing, Metals and Plastics Publications, Inc., New Jersey, 1977, pg. 180.

2. J. G. Poor, Somers, and G. B. Rynne, U. S. Patent 3,730,855.

3. G. F. Hsu and M. M. Beckwith U. S. Patent 3,729,394.

TABLE I

Cadmium (as metal)	2.6 to 4.8 oz./gal.
Sodium cyanide	10.4 to 21.6 oz./gal.
Sodium hydroxide	1.8 to 8.0 oz./gal.
Sodium carbonate	4 to 6 oz./gal.
Addition agent	Required

TABLE II

CADVERT* Acid Sulfate Cadmium Plating Bath

	1 Liter	1 Gallon
Cadmium Oxide	17 g	2.25 oz.
Sulfuric Acid, Sp.Gr. 1.84	31 ml	4 fl. oz.
CADVERT No. 374	30 ml	4 fl. oz.
CADVERT No. 375	3 ml	0.4 fl.oz.
Water to make	1 liter	1 gallon

*Product of 3M Co., Pat. No. 3,998,707
Pat. No. 4,045,305

TABLE III

Operating Conditions	Range
Cadmium Metal	11.25 to 18.75 g/l (1.5 to 2.5 oz./gal.)
Free Sulfuric Acid, Sp. Gr. 1.84	23.4 to 31.2 ml/l (3.0 to 4 fl. oz./gal.)
Temperature	18 to 27° C. (65 to 80° F.)* *Lower acid and temperature are favored for plating on carbo-nitrided steel and cast iron.
Cathode Current Density	Rack: 0.5 to 2.5 A/dm^2 (5 to 25 A/ft.^{2}) Barrel: 0.2 to 1.5 A/dm^2 (2 to 15 A/ft.^{2}), calculated on the basis of the total area of the load.
Voltage	Rack Plating: 6 to 12 volts Barrel Plating: 4 to 18 volts
Agitation	Cathode rod agitation (rack plating) - 1 to 2 meters (3 to 2 meters (2 to 6 feet) per minute.

TABLE IV

Equipment Requirements

Plating Tank		Steel, lined with PVC or rubber. Polyethylene or polypropylene.
Anodes		Cadmium slab anodes in combination with carbon anodes.
Cooling Coil		Teflon tube, teflon coated copper, titanium coil, external heat exchanger of glass or graphite.
Filter		One or two turnovers per hour desirable. Acid resistant components.
Rectifier	Rack:	To 12 volts, 5% maximum ripple
	Barrel:	To 18 volts, 5% maximum ripple

Composition Range of Cyanide Baths

Cadmium (as metal)	2.6 to 4.8 oz./gal.
Sodium cyanide	10.4 to 21.6 oz./gal.
Sodium hyroxide	1.8 to 8.0 oz./gal.
Sodium carbonate	4 to 6 oz./gal.
Addition Agent	Required

CADVERT*
Acid Sulfate Cadmium Plating Bath

	1 Liter	1 Gallon
Cadmium Oxide	17 g	2.25 oz.
Sulfuric Acid Sp.Gr. 1.84	31 ml	4 fl. oz.
CADVERT No. 374	30 ml	4 fl. oz.
CADVERT No. 375	3 ml	0.4 fl. oz.
Water to make	1 liter	1 gallon

* Product of 3M Company, Pat. No. 3,998,707
Pat. No. 4,045,305

Bath Composition

Cadmium metal 15 g/l (2.0 oz./gal.)
Free Sulfuric Acid, Sp.Gr. 1.84 23.4 ml/l (3.0 fl.oz./gal.)
plus organic additives

Operating Conditions	Range
Cadmium Metal	11.25 to 18.75 g/l(1.5 to 2.5 oz./gal.)
Free Sulfuric Acid, Sp. Gr. 1.84	23.4 to 31.2 ml/l(3.0 to 4 fl.oz./gal.)
Temperature	18 to 27° C (65 to 80° F.)*

*Lower acid and temperature are favored for plating on carbo-nitrided steel and cast iron.

Cathode Current Denisty	Rack: 0.5 to 3.0 A/dm^2 (5 to 30 A/ft.^{2}) Barrel: 0.2 to 1.5 A/dm^2 (2 to 15 A/ft.^{2}), calculated on the basis of the total area of the load.
Voltage	Rack Plating: to 9 volts Barrel Plating: to 18 volts
Agitation	Cathode rod agitation (rack plating) 1 to 2 meters (3 to 6 feet) per minute

Advantages and Disadvantages

Disadvantages

1. Acid resistant equipment required.
2. May require special chromating solutions. Cathode efficiency slightly lower than cyanide bath.
3. Less throwing power.

Advantages

1. Simple economical waste treatment:
    - No cyanide
    - No ammonium ions
    - No chelators
    - No complexing agents
2. Less dragout of cadmium metal.
3. No carbonate formation.
4. Nickel strike not required on stainless steel.

Equipment Requirements

Plating Tank	Steel, lined with PVC or rubber. Polyethylene or polypropylene.
Anodes	Cadmium slab anodes in combination with carbon anodes.
Cooling Coil	Teflon tube, teflon coated copper, titanium coil, external heat exchanger of glass or graphite.
Filter	One or two turnovers per hour desirable. Acid resistant components.
Rectifier Rack:	To 9 volt
Barrel:	15 volt for plating mild steel 18 volt for plating case hardened carbonitrided or cast iron parts.

Analysis and Control

Cadmium - Volumetric analysis
Sulfuric acid - Volumetric analysis

CADVERT No. 375 - 120 to 240 ml (4 to 8 fl.oz.) per 1000 amperes of operation
CADVERT No. 374 - Add at rate of 10% by volume of sulfuric acid added

Hull cell test provides additional control.

Waste Treatment

Raise pH of effluent to 10.5 - 11.0

Use sodium hydroxide or hydrated lime

Remove precipitated cadmium by filtration, settling or decantation.

Filtrate cadmium concentration less than 0.5 ppm.

A New Non-Cyanide Electroplating Bath

MR. GUIO: Ralph Guio from Amphenol Connector Operations. Did you try pulse plating with the acid-type cadmium?

MR. JORCZYK: No, we didn't.

MR. GUIO: We have done some work with this particular type of bath. We found that the acid-type cadmium bath is readily adaptable. Pulse plating gives a finer grain and preferential deposition compared with the cyanide-type bath.

MR. JORCZYK: The bath we have produces a bright deposit which is fine grained, but we will keep your point in mind. Thank you.

MR. VAALER: Luther Vaaler, Battelle, Columbus. Do you have a chloride cadmium bath? If you don't, why not?

MR. JORCZYK: Not at this time. Perhaps in the future some work will be done with that. Chlorides using insoluble anodes would evolve chlorine gas, which would not be desirable.

MR. BOOKER: Jonathan Booker from Brush Wellman in Cleveland, Ohio. I noticed that many speakers today have talked about both rack plating and barrel plating. Would this bath be sufficient for continuous strip plating?

MR. JORCZYK: It probably could be developed to that, but most of our efforts have been in steel and in barrel plating. But as time allows, we certainly will look at that area.

Alternative Materials and Processes

Session IV

Wednesday Afternoon 2:55

BONDED SOLID FILM DRY LUBRICANTS AS AN ALTERNATIVE TO CADMIUM ELECTROPLATING

Theodore M. Pochily
Benet Weapons Laboratory
Watervliet Arsenal
Department of the Army
Watervliet, New York 12189

Bonded solid film dry lubricants have gained wide acceptance in recent years. These materials are used in many areas of military weapons development and production. The evolution of dry lubricants from a rather a minor role to a key lubricant in critical application has been rather startling. This increase in application can be directly related to an improved performance in the area of corrosion protection.

Their use as a corrosion barrier with the benefit of good lubricity increased the scope of application for the ordnance engineer. Studies resulting from these early findings indicated the possibility of replacing some of our metallic coatings with a dry film lubricant. Carbon steel panels were plated with .002 inches of nickel, electroless nickel, cadmium and chromium. Additional panels were coated with less thatn .001 inches of DFL after a base coating of zinc phosphate. Results of salt spray tests proved the dry film coating superior to the nickel chromium and electroless nickel coatings and at least equal to cadmium after 960 hours exposure. Selective components previously coated with nickel and chromium are now sprayed with a DFL with excellent results. Equal results could be expected in the case of cadmium plating.

The replacement of cadmium by a DFL has merit when several areas are considered. The elimination of hydrogen embrittlement associated with cadmium plating, will be a direct benefit. The disposal of toxic chemicals and vapors such as cadmium, cyanide and chromates will not be necessary and the costly pollution control apparatus would not be required. Additional economic benefits can be realized when the need for expensive plating equipment and the energy required to heat the processing equipment is eliminated.

Preceding page blank

BONDED SOLID DRY FILM LUBRICANTS AS AN ALTERNATIVE TO CADMIUM ELECTROPLATING

Theodore M. Pochily
Watervliet Arsenal
Department of the Army

Solid bonded dry film lubricants (DFL) have gained wide acceptance in recent years. They are used on many principal systems and components that comprise the Army's conventional weapons inventory. These materials have emerged from a limited role several years ago to a prominent function in providing lubricating in many critical applications. The properties of dry film lubricants are unique in that they have the ability to function at temperatures, pressures and aggressive environment beyond that of conventional lubricants. The advantages of a solid dry film material with respect to a low frictional - possibly long life oil or grease can be states as follows:

1. Solid dry films may be used effectively at higher and lower temperatures.
2. May be used in environments and atmospheres that would contaminate or degrade an oil or grease.
3. A dry film will suffice and reduce the requirement for oil feed systems and associated equipment if bearings do not require cooling.
4. It has the ability to be put on as an adherent film - will not be displaced by excessive pressures.
5. Has a good resistance to abrasive forces.
6. Has the ability to impart a corrosion barrier to the substrate.

Disadvantages such as the following are recognized:

1. Because of the solid contact - wear of the coating is noted.
2. Solids cannot act as coolants.
3. Coefficients of friction generally are higher than that obtained with the conventional lubricants.

4. There is a finite life of the coating but normally this life will exceed the life requirement.

Considering the advantages of these materials in providing lubrication to reduce friction and wear, several areas of applications should be recognizable. Some examples might be:

1. Light and moderately heavy bearings.
2. Sliding motion under moderate to heavy loads.
3. Temperature range - 300°F to 500°F.
4. Mechanism lubricated for life.
5. Mechanisms exposed to a range of climatic condtions varying from dust to snow and ice, salt laden atmospheres, corrosive chemical environments.
6. Components stored for long periods of time.
7. Parts exposed to high temperatures, with periodic disassembly required.
8. Mechanism that will malfunction when contamination of fluids or greases occur.

From the viewpoint of the military and the personnel responsible for the continuous operation of vehicles and weapons, these dry film lubricants have the ability to resolve many problems concerning wear, lubrication and corrosion.

It is the objective of this presentation to briefly outline the successful application of DFL, principally those compounded with thermosetting, resins conforming to Mil-L-46010. The makeup of these compounds follow a general compositions; an organic resin normally epoxy and/or phenolic. lubricating inorganic fillers such as molybdenum disulphide and graphite and acid neutralizers. These materials are blended with a suitable solvent that allows for a consistency compatible with whatever method of application is desirable.

It must be noted, that these materials have not nor will they replace conventional lubricants in many applications. What is important, however, is to recognize that the dry film lubricants extends the range of lubrication technology as well as the range of operation in aggressive environments.

The ability to function in environments that normally corrode the basis metal can, to a large extent, be attributed to a barrier resulting from the organic resin. It was this ability, a means of providing a corrosion barrier with no sacrifice of lubricating properties that intrigued the weapons design engineer. The problem of corrosion is and has been of significant importance to the military services. The effectiveness and functionality of weapons and systems have been deleteriously effected as a result of improper or minimal corrosion protection.

During the early period of D.F.L. investigation at the Watervliet Arsenal, the attitude of the engineers were concerned only with the replacement of one form of lubrication with another. This was a normal assumption and in most cases these D.F.L. materials performed admirably. Included in these applications were two major components, the 120mm breech block assembly (#1) and at the T206 firing lock (#2). Both components were completely coated and resulted in a decrease in the force required to actuate them.

The next component (slide #3) a 20mm feed mechanism functioned well under all environmental conditions. However, the corrosion noted here occurred during normal storage and presented an unacceptable situation to the ordnance engineer. Also revealed at this time by several other agencies, was the fact that corrosion products have been found on surfaces coated with dry film lubricants. This knowledge stimulated investigations at several manufacturers and user laboratories with the result that the major contributor to the corrosion problem was isolated. The commercial product used by Watervliet during this period was known to have a high percentage of graphite. It was known that graphite relies on the moisture in the atmosphere for assistance in lubrication. It was also known that when graphite was tested under vacuum, the lubricating properties of the material no longer existed but become damagingly abrasive. Consequently, it was concluded that the D.F.L. compound in addition to lubricating also promoted corrosion to the base metal.

Several lubricants both conventional and bonded solid dry film were evaluated for wear life and corrosion protection. The Falex Wear Tester using a 1000 lb gauge load and a salt spray chamber with an atmosphere of 5% NaCl at 95°F were used for these determinations. The results shown in slide #4 are self explanatory indicating excellent performance in bath catagories for the .0005" inches (.5 mil) DFL coating.

The efforts of the personnel in the dry film field were directed toward a resolution of this problem. The results of these efforts were successful to a point that the entire philosophy of dry film lubrication was changed. Now, it was realized that, in addition to providing lubrication, these compounds would be required to protect the base metal from corrosive forces.

A comparative evaluation of available D.F.L. material conforming to specification Mil-L-8937 and Mil-L-46010 appeared to be desirable at this time. The basic difference in the two specifications is concerned with graphite as a lubricant. Mil-L-46010 prohibits the use of graphite while the other does not. The data in slide #5 reflects the superior wear and corrosion resistance of the graphite free DFL.

The perfect merger of these properties was expected to increase the field of application. The possibility of providing a barrier to corrosion and to lubricate moving components with a coating less than .001 inches thick was intriguing, and the elimination of comparatively heavy electrodeposits, used as corrosion and wear protection, was an advantage that had to be considered. The validity of this pronouncement is quite evident today by the extensive acceptance of dry film lubricants as a corrosion barrier coating with a lubricant. With this type of information, it was more easy to convince the design engineer of the value of these materials. During this period, a severe corrosion problem was found in the storage and field use of the 105mm M103 (Slide 6). Extensive corrosive attack was evident on the recoil slide surface of this weapon despite normal field maintenance.

This surface in several earlier gun models, was chrome plated for wear and corrosion protection and lubricated with conventional lubricants. The susceptibility of chromium electrodeposits of .005 inches thick to corrosion is illustrated in the next slide, slide #7.

Two badly corroded areas are noted on the recoil slide surface of this 90mm M41 weapon.

Concurrent studies relating to the above problems and to the lubrication of the new 155mm M126 were in progress. The new weapon was autofrettaged throughout the bore and due to the presence of tensile residual stresses at the O.D. induced through the autofrettaged process, no chemical acid treatment of the tube was permitted on the outside surface. The use of a bonded solid film lubricant to the recoil slide surface presented a viable solution to the lubricating problem of this weapon. After 2000 rounds and six month outdoor exposure to the varying climatic conditions of the Great Lakes area, no evidence of wear or corrosion was noted. This is illustrated in the next slide where the expected burnished surface is noted (Slide #8). With one problem solved others were generated during extended firing sequence.

The muzzle end of a gun that is mounted on either a tank or enclosed self propelled vehicle contains two necessary components. The muzzle break which is used to reduce the recoil forces when the gun is fired and the bore evacuator which is necessary to evaluate the noxious propellent gases from the tube during firing. A deposit of propellent residue, carbon and corrosive gases create a corrosion problem between these components and the mating threads or the weapon. The application of a dry film lubricant resolved this problem and reduced the dissassembly of time by approximately four hours. The subject areas are shown in this slide (#9) a comparison of a corroded area and the D.F.L. coated area are obvious.

Slide #10 shows the bore evacuator in place and Slide #11 illustrates the extent of dry film coating on 3 155mm tubes.

The acceptance of the D.F.L. coating as a corrosion barrier was further demonstrated when an experimental 105mm when all mating surfaces, all internal components such as springs, cams, extractor, etc. were processed with a dry film lubricant. The entire weapon assembly was towed through the ocean surf and further exposed to the salt laden environment for a two week period. This exposure would normally corrode the weapon whereby activation of the system would be difficult if not impossible. This was not the case, and this howitzer continues to function with a minimum of maintenace. Slide #12 shows the weapon prior to acceptance by the Marine Corps.

It must be recognized that corrosion control is a prerequisite to proper lubrication since corrosion destroys both the surface and the lubrication of that surface.

The encouraging results of these applications were at a level that the anxieties created by the previous failures due to excessive corrosion were quickly forgotten to the point that the D.F.L. coatings were looked on with favor when a corrosion problem was evident.

At this point in time the application of D.F.L. materials was primarily a substitute for conventional lubricants. However, the replacement of anodic and conversion coatings as well as black oxide treatment was accomplished during this period. The excellent performance with respect to wear corrosion and lubrication led to a reevaluation of some of our metallic coatings in our metal finishing system. Results of this reappraisal led to the replacement of several electrodeposited metallic coatings. As an example, the D.F.L. coatings replaced a .002" nickel coating on the extender tube of the Marine Drive Assembly. This unit is used to propel bridge components through water whenever the need for a portable bridge is required. Chromium deposits which used as a wear and corrosion resistant coating have been either replaced or augmented with a dry film lubricant (Slide #13).

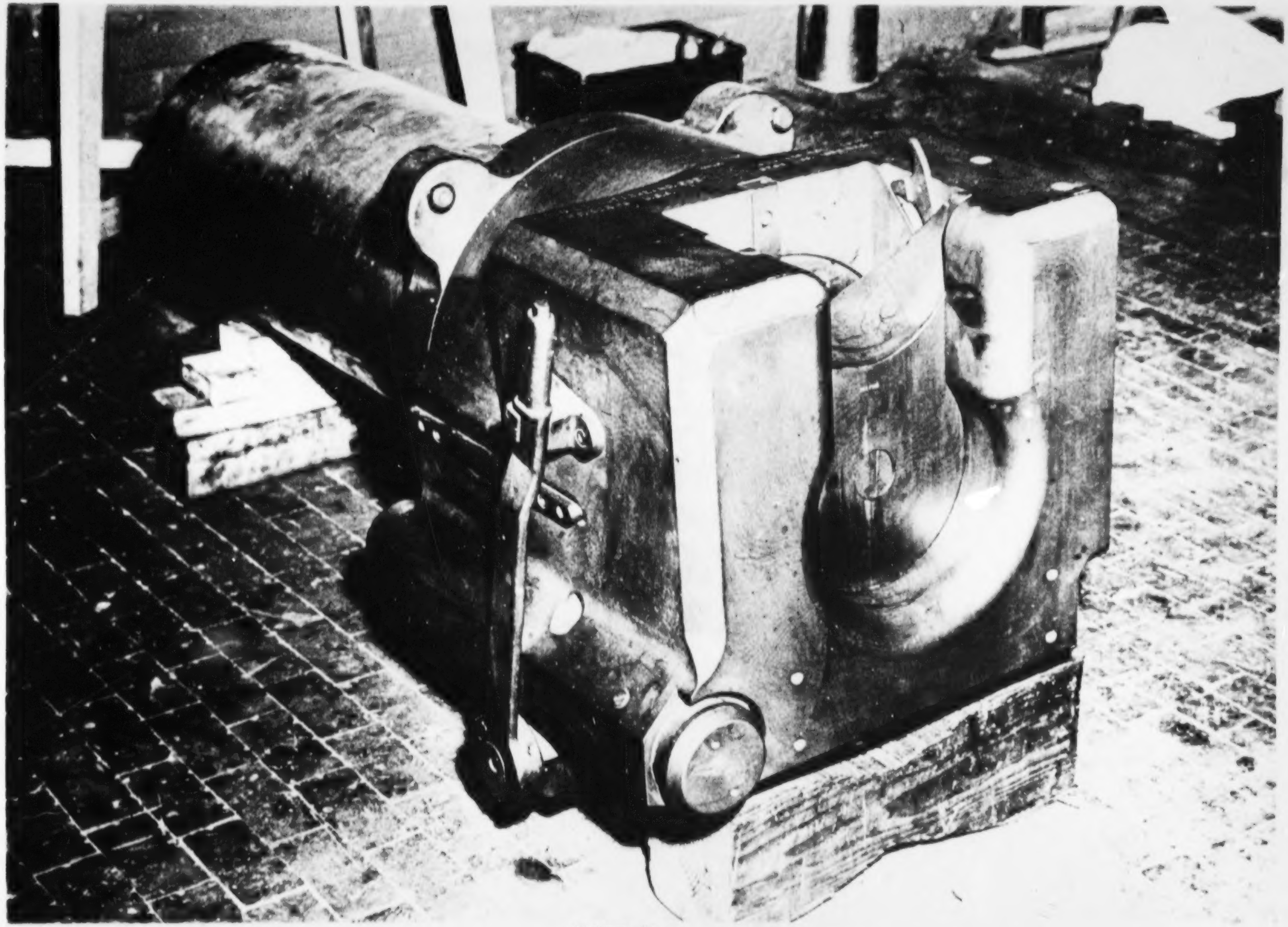
The last slide (Slide #14) indicates the excellent corrosion resistance of the D.F.L. material used at the Watervliet Arsenal. The salt spray resistance as compared to the deposited .002" coatings of chromium, nickel, electroless nickel is considerably better. The performance against the chromated treated cadmium deposit is comparable at 960 hours.

To summarize what has been presented; the DFL coatings has given the design engineer an alternative to several metal finishing systems. At the Watervliet Arsenal, after a comprehensive comparative evaluation of selected components and systems the following changes have occurred. The DFL covered under Specification Mil-L-46010 has replaced in many instances:

1. Conventional lubricants
2. Phosphate conversion coatings
3. Black oxide coatings
4. Chromate conversion coatings
5. Anodic coatings on aluminum, magnesium and titanium
6. Enamel and lacquer paint systems
7. Copper deposits when used as a lubricant
8. Lead deposits when used as a lubricant
9. Nickel coating when used as a corrosion barrier
10. Electroless nickel when used as a corrosion barrier
11. Chromium deposits when used as a lubricant and corrosion barrier

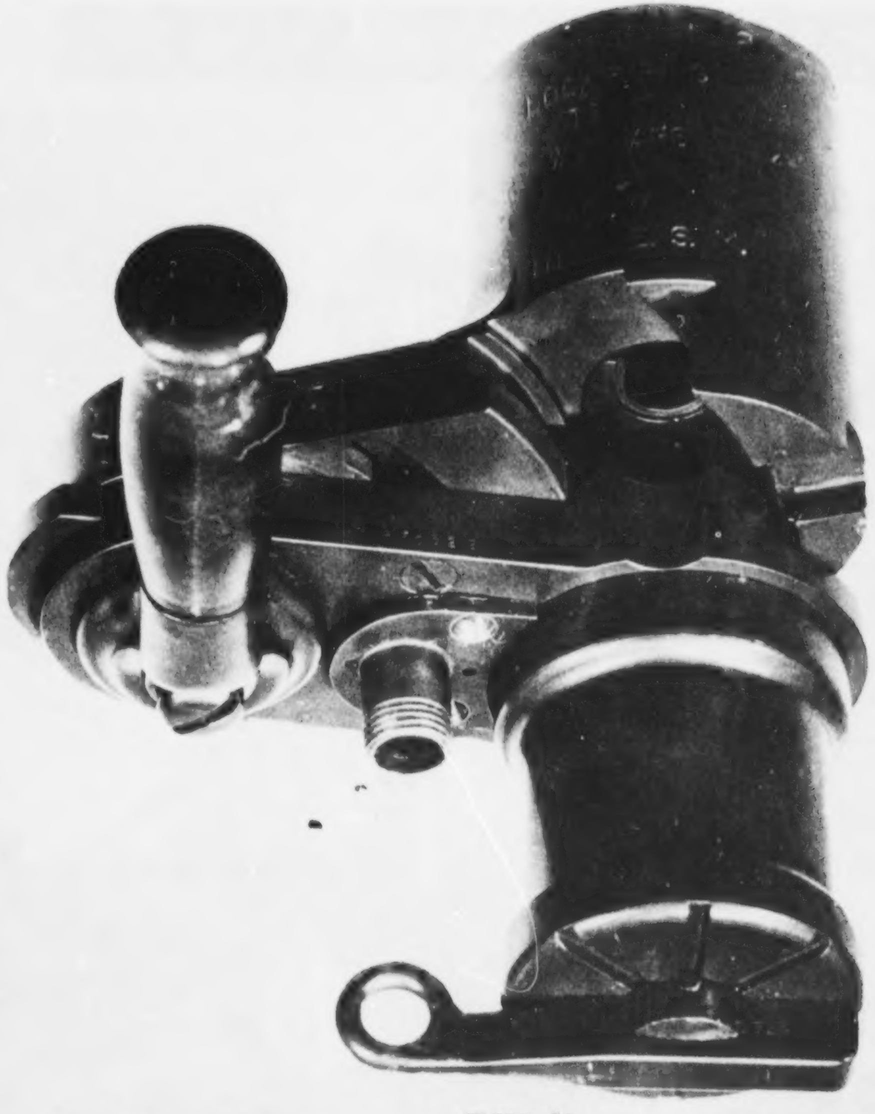
Several benefits of this system are quite apparent. The ease of application, simplification of processing equipment, absence of effluent pollutants and a minimum of exposure to noxious and toxic fumes to the operator. Other benefits not obviously as apparent are concerned with the mechanical and physical properties of the basis metal. Included would be phenomena such as hydrogen embrittlement from chromium and cadmium plating, the intermetallic alloying of tin due to the diffusion of the liquidified coating, intergranular corrosion when lead is used as a lubricant under high pressures and the concern for galvanic corrosion would not be a factor when dissimiliar metals are coupled.

The information shown on the last slide clearly indicates the excellent salt spray resistance of the DFL material and was used as a basis for the replacement of some of our metallic coatings. It is, at the present time the basis of a submitted Arsenal program relating to the elimination of our cadmium plating facility. The DFL coatings may not suffice in all instances but a review of the requirements of each component and its relationship to the over all weapons system, will find these materials more than acceptable. It is the intent of this paper to present those areas where a successful application has been realized and to introduce the DFL materials as a viable replacement for electrodeposited coatings such as nickel, chromium and cadmium.



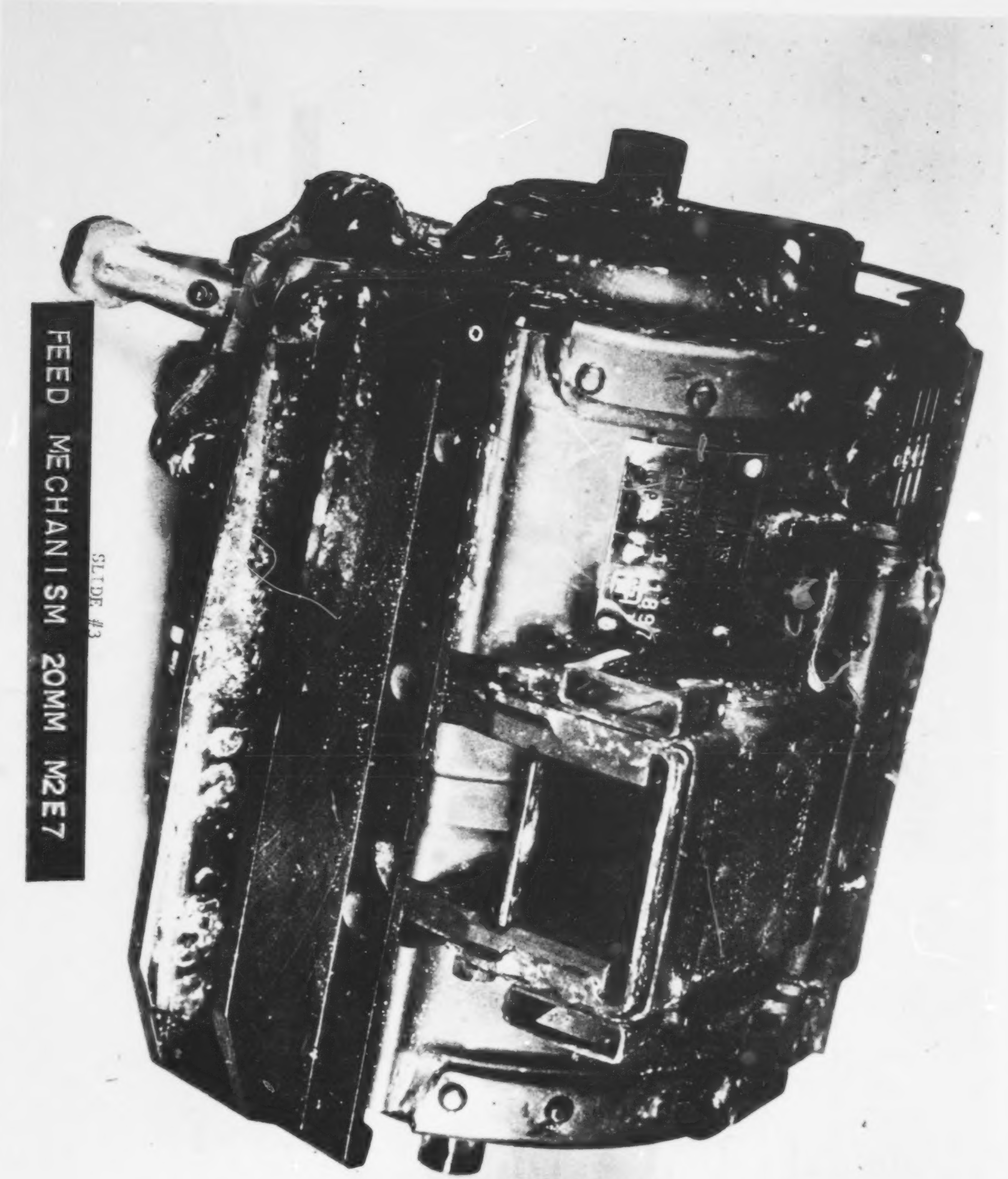
SLIDE #1

DRY FILM COATED 120MM BREECH MECH.



SLIDE #2

DRY FILM COATED T206 FIRING LOCK



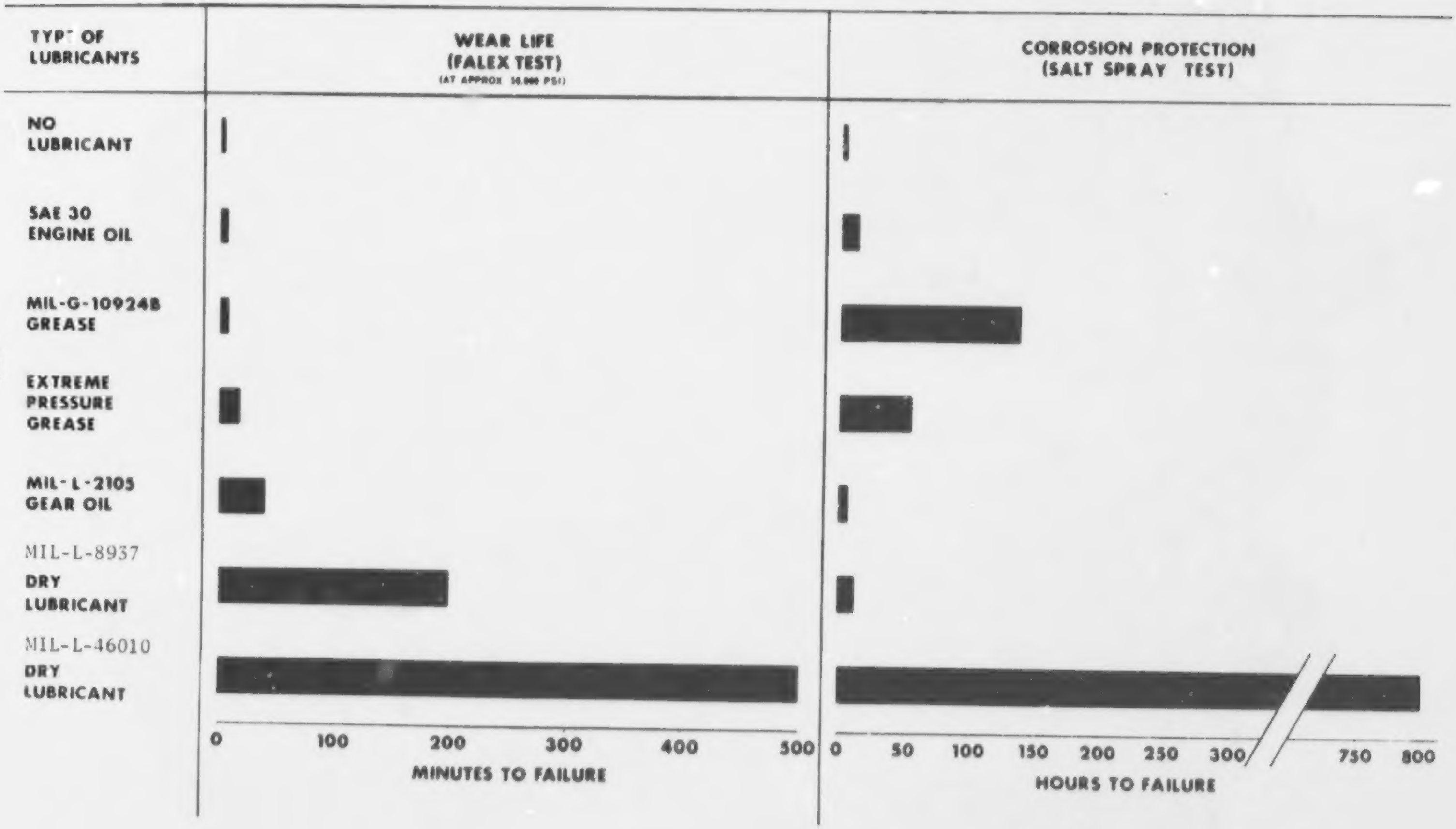
FEED MECHANISM 20MM M2E7

SLIDE #3

SLIDE #4

EFFICIENCY OF LUBRICANTS

(WHEN APPLIED TO PHOSPHATIZED STEEL)



SPC 103

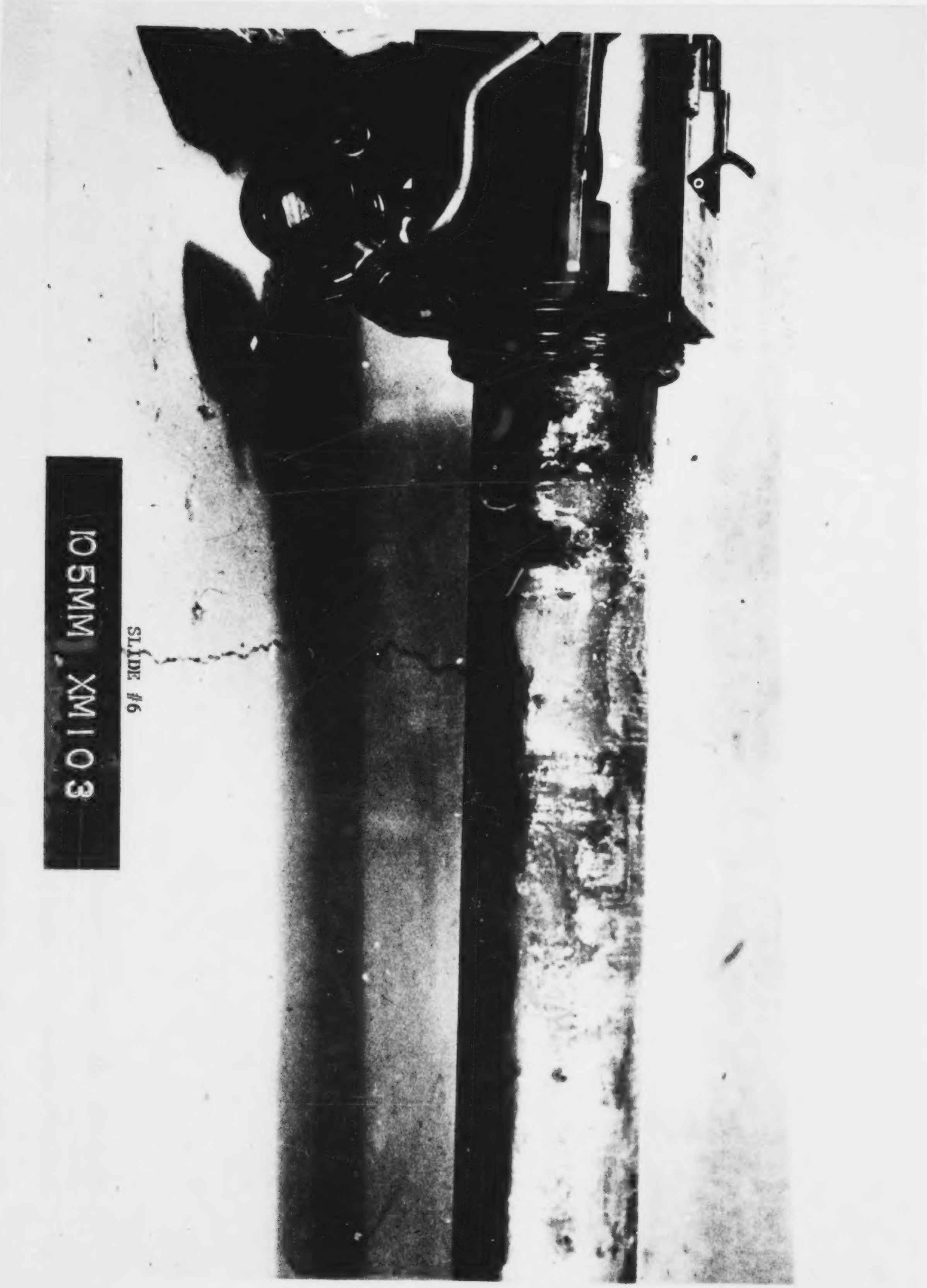
COMPARATIVE TEST DATA
SOLID FILM LUBRICANTS
SLIDE #5

PRODUCT	MANUFACTURER	SALT FOG: (HOURS TO FAILURE)	FALEX WEAR LIFE (MINUTES)	FALEX E.P. FAILURE (LOAD LBS.)
A (Meets MIL-L-46010)	S	850	680	2750
* D	A	<4	80	3250
* S	D	16	240	3250
* M	A	<4	230	3250
* L	E	65	60	2750
* 6	E	4	136	3125
* H	H	67	90	2875
* S	H	<4	168	3125
* N	N	2	84	3250
* P	P	4	210	3375

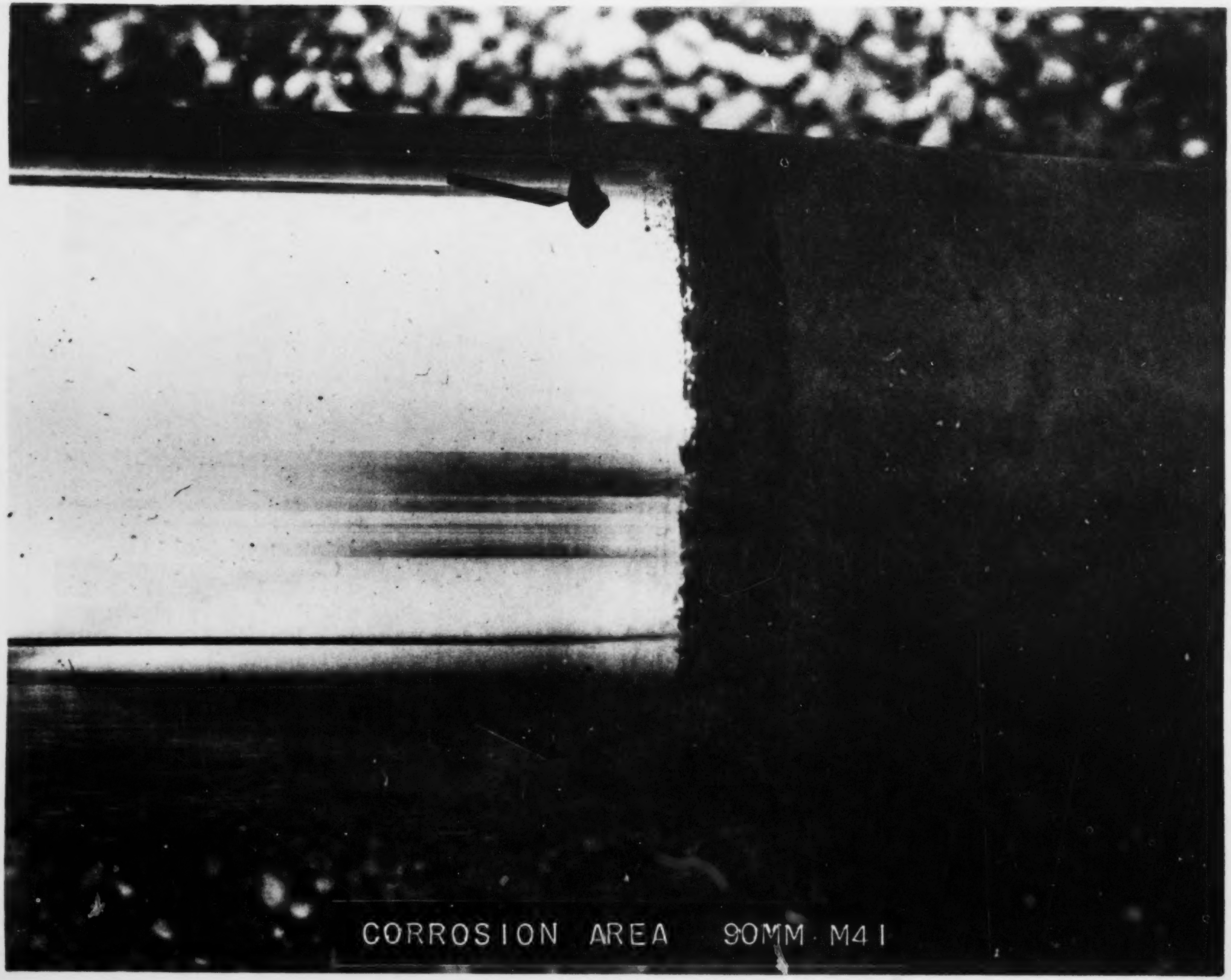
* MIL-L-8937 (ASG) Qualified Products

Surface Preparation: Grit Blasted & Zinc Phospated

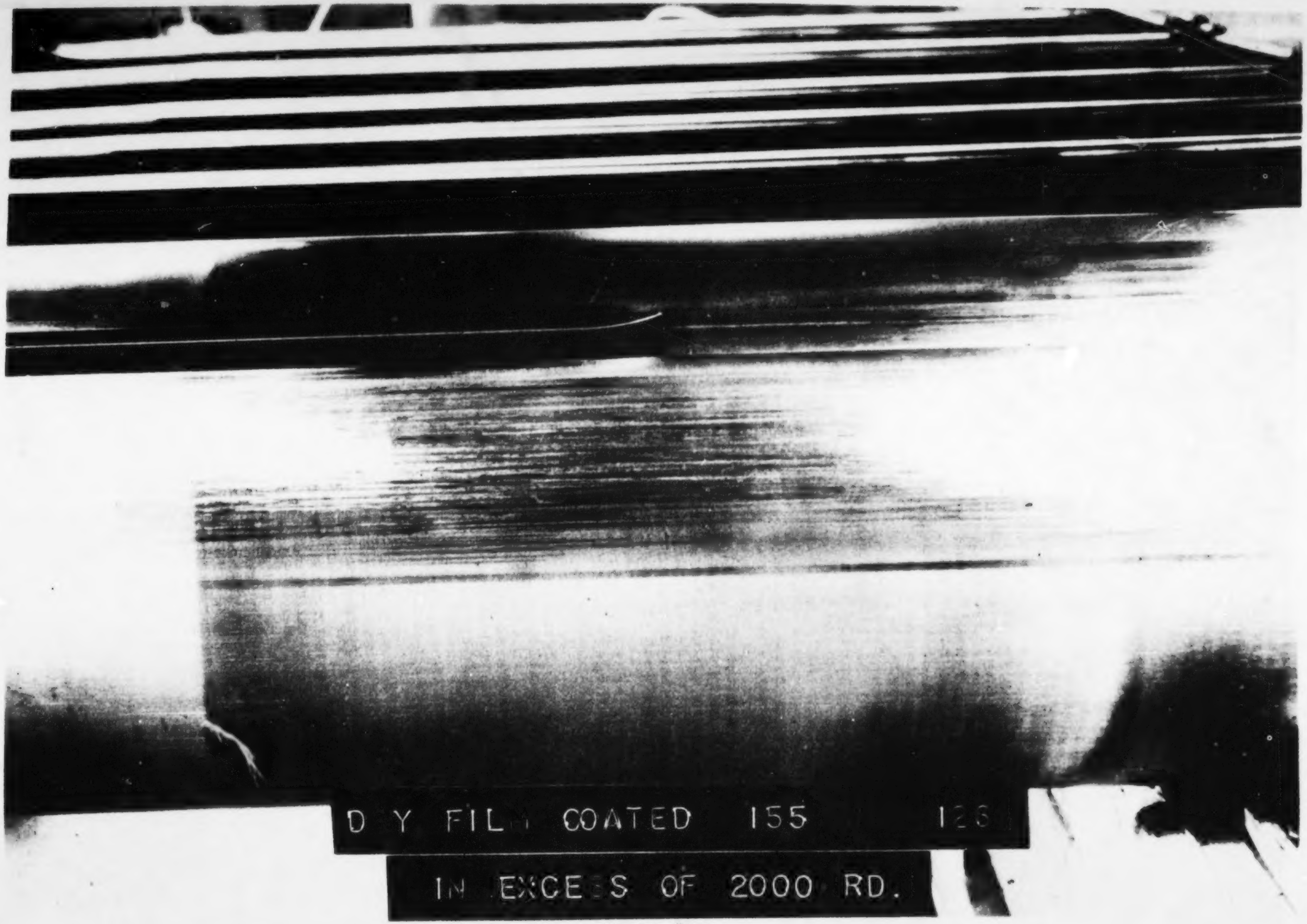
Film Thickness: .0005 ± .0001 inches



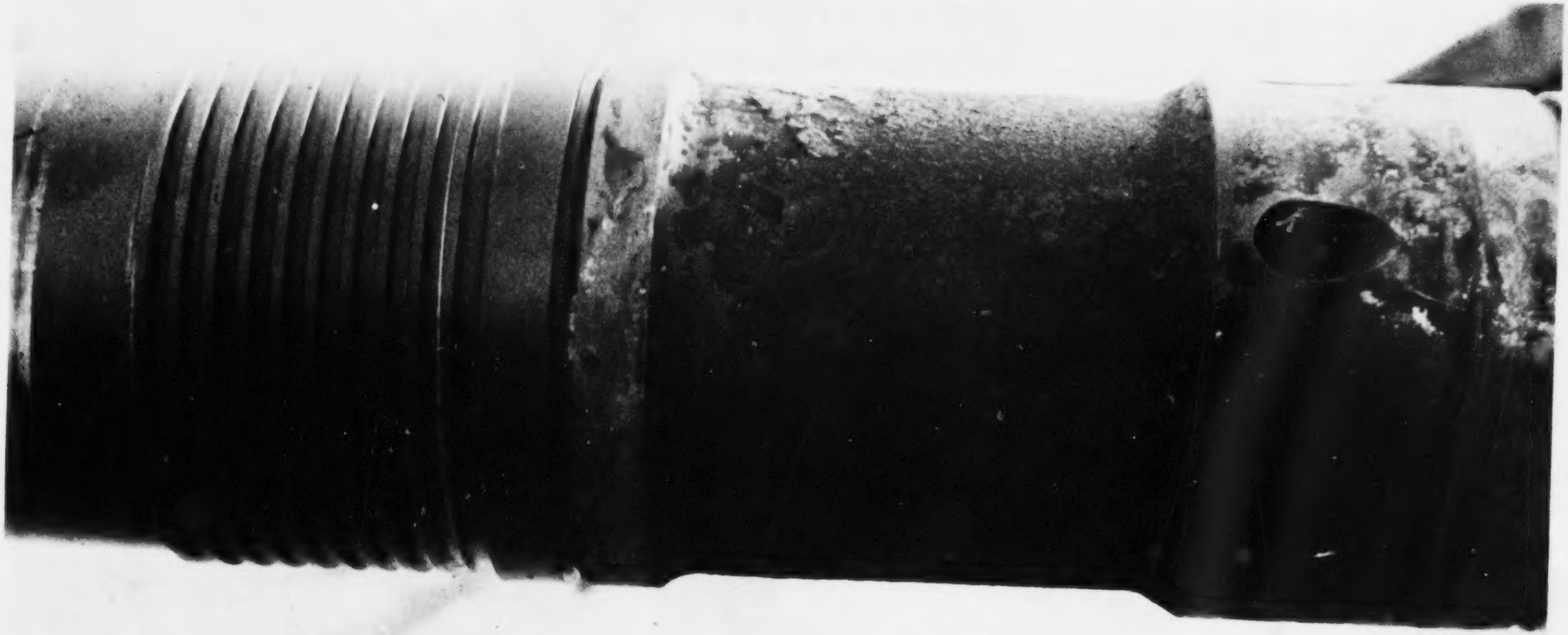
SLIDE #6



SLIDE #7

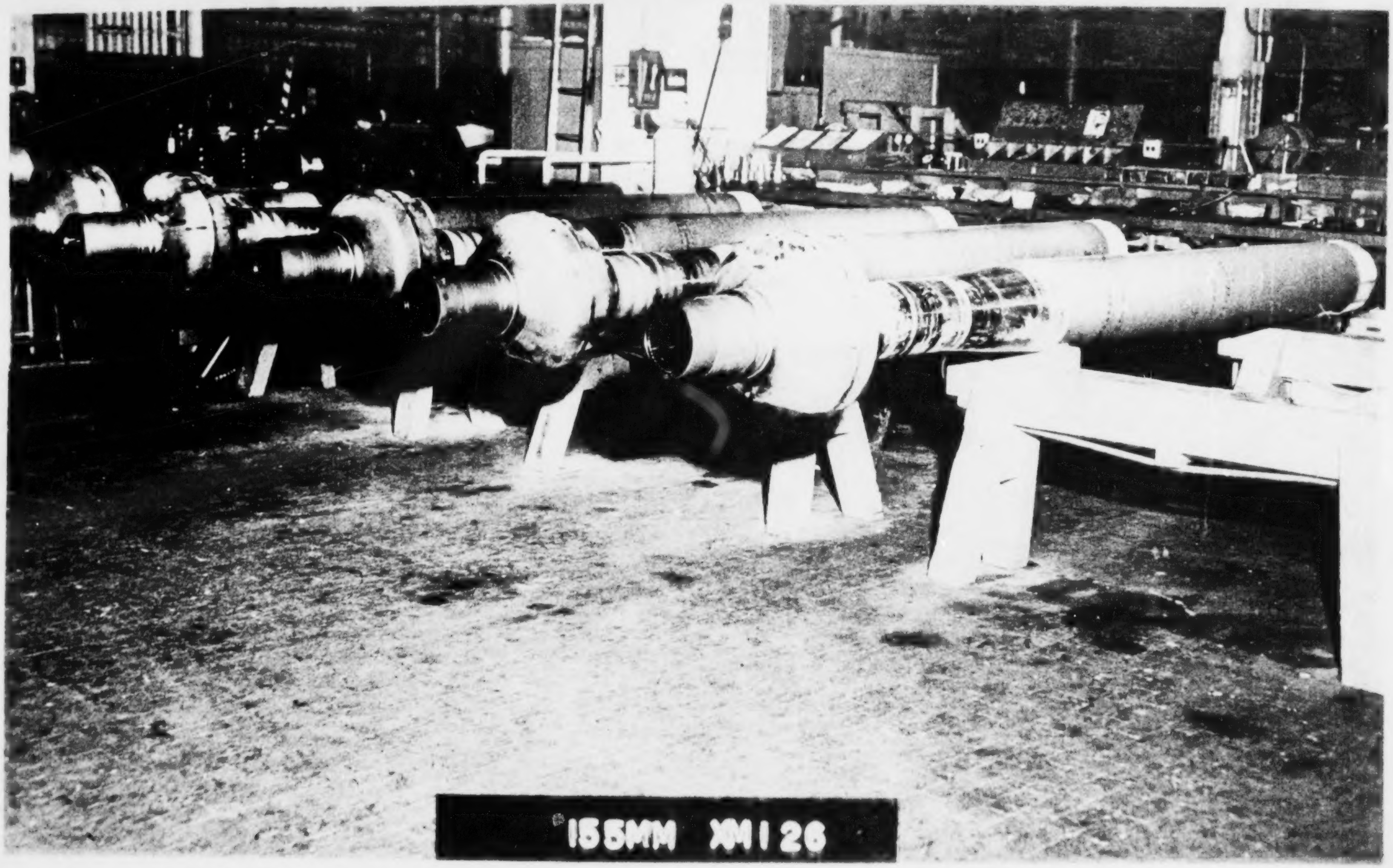


SLIDE #8

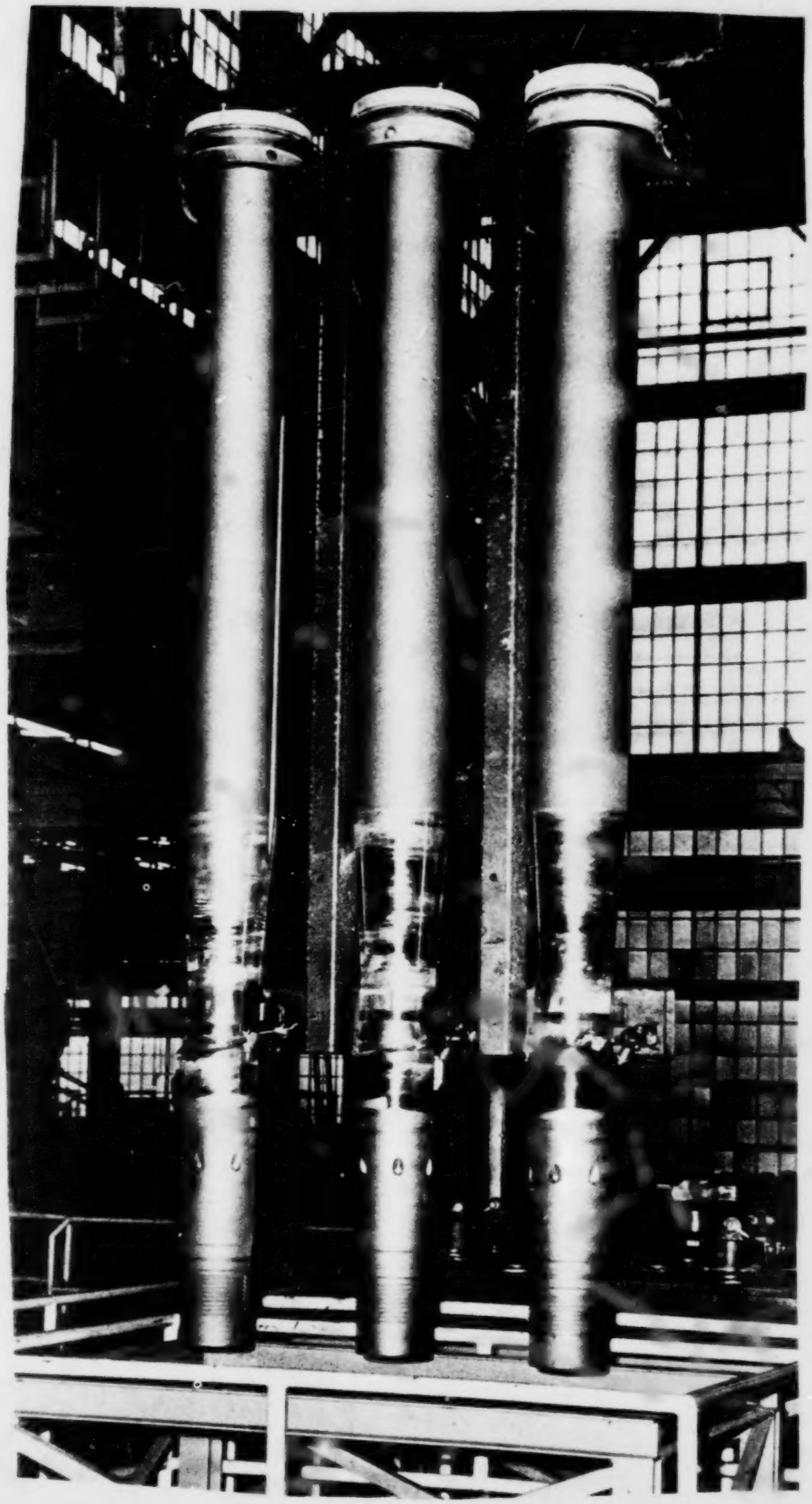


CORRODED AREA UNDER BORE EVACUATOR 155MM

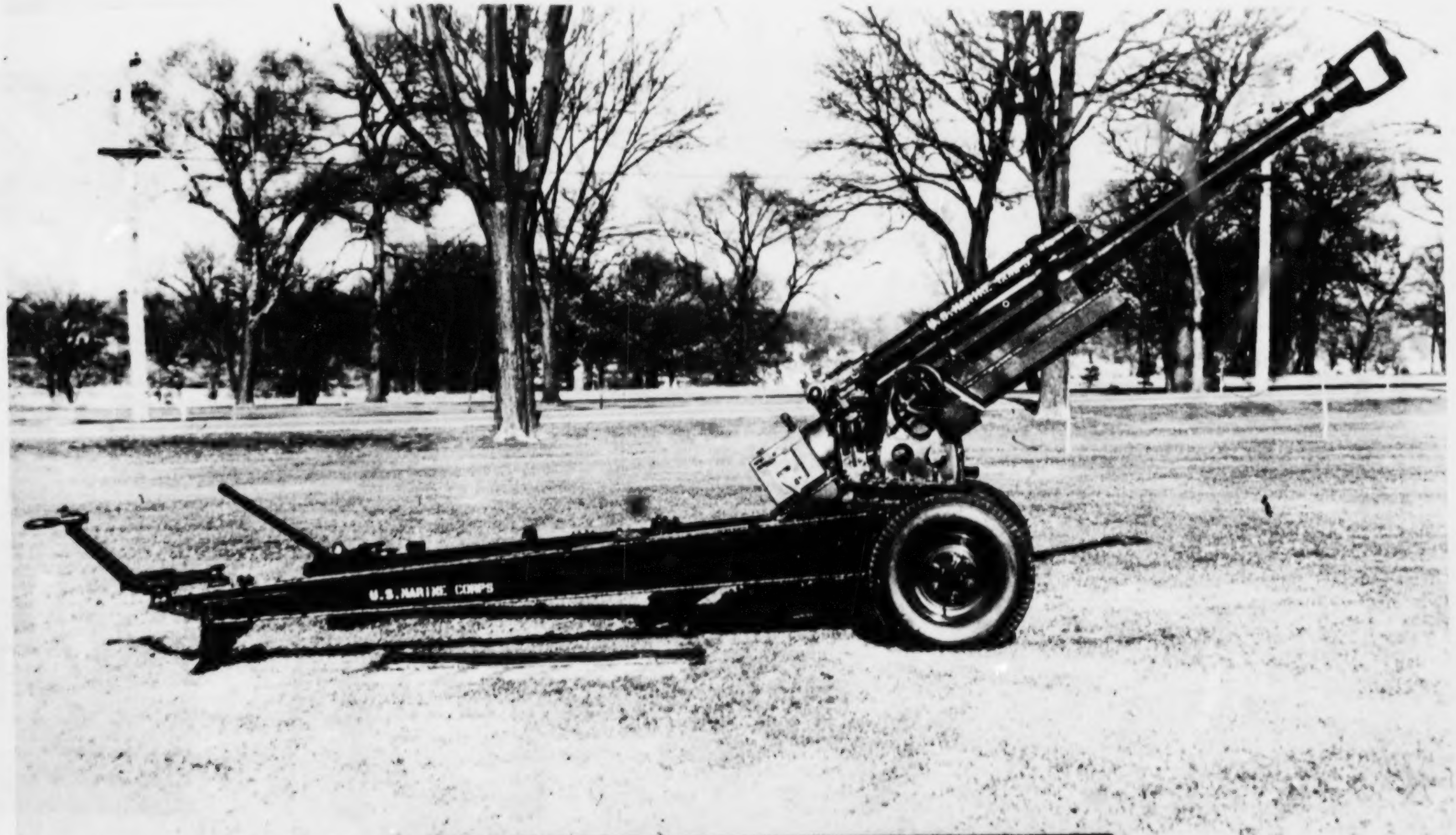
SLIDE #9



SLIDE #10

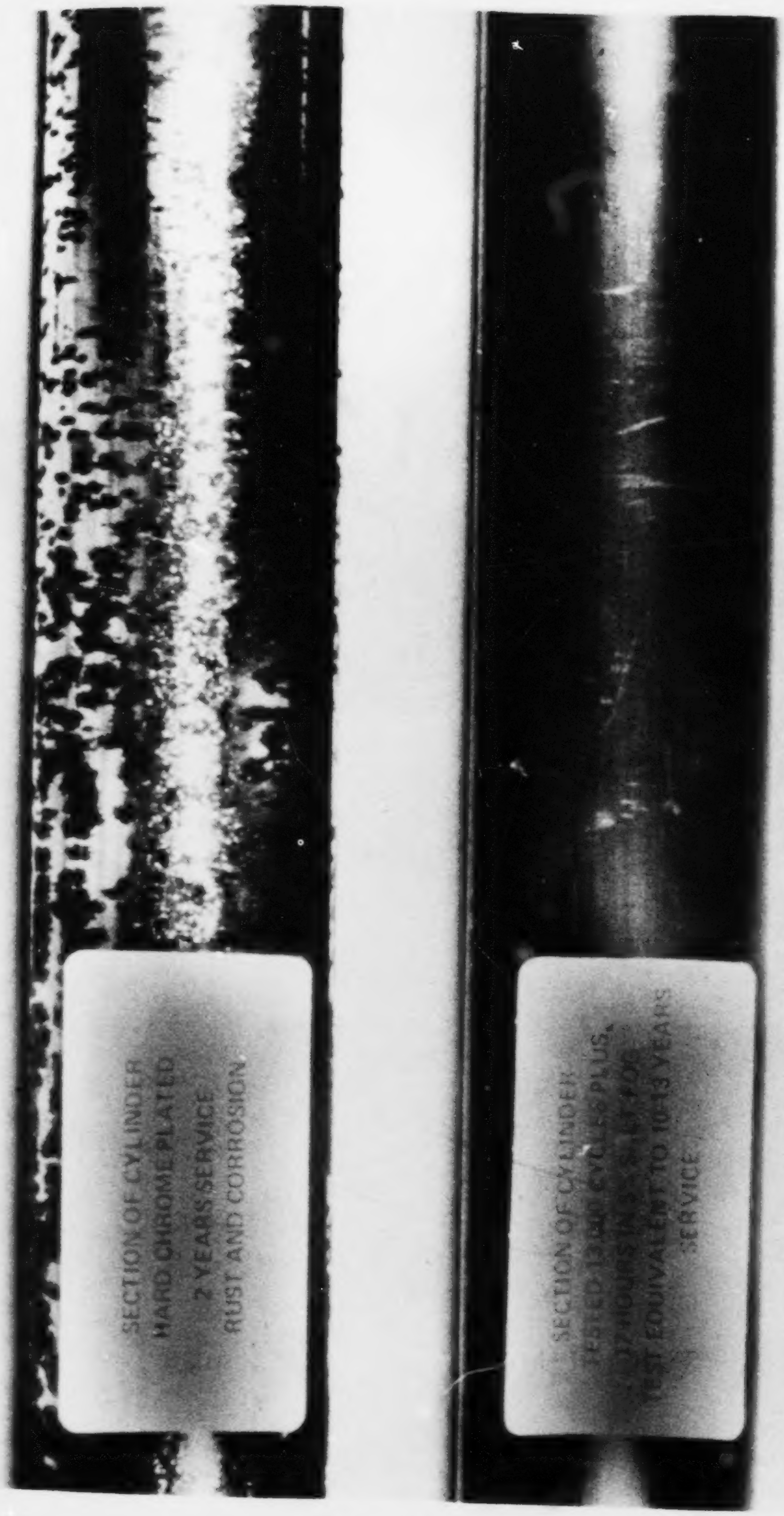


SLIDE #11



MARINE 105MM HOWITZER

SLIDE #12



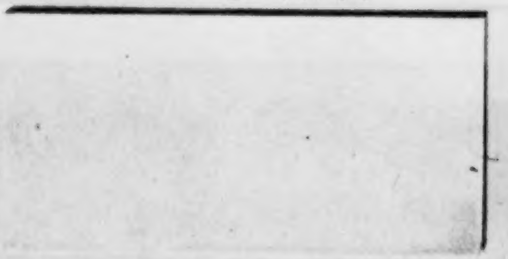
SLIDE #13

Reproduced from best available copy.

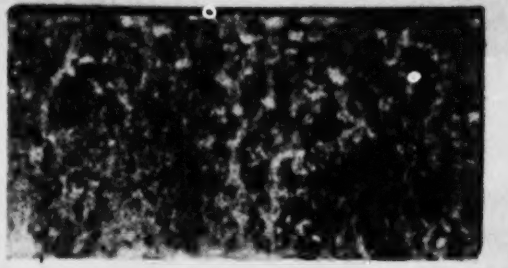
COMPARISON: DRY FILM LUBRICANT TO VARIOUS PLATINGS AFTER 960 HRS. IN 5% SALT SPRAY

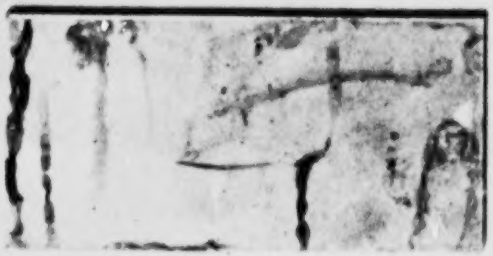
SLIDE #14

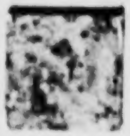
D.F.L – SANDSTROM 9A – 1/2 mil.


CADMIUM PLATE – 2 mils.

NICKEL PLATE – 2 mils.


D.F.L. – DOW CORNING 3400 – 1/2 mil.


ELECTROLESS NICKEL PLATE – 2 mils.


CHROME PLATE – 2 mils.

Bonded Solid Film Dry Lubricants as an Alternative to Cadmium Electroplating

MR. HRATKO: Bill Hratko, Sunstrand. In the elimination of chromates, anodizing, and phosphating, how do you prepare various substrates like steel?

MR. POCHILY: A lot of the weapons that we work with are autofatigued. That means they are stressed to improve the fatigue and the weld life.

In preference to using a zinc phosphate coating, we just vapor hone.

The 155's are vapor honed, and there is no zinc phosphate underneath those. If you want a longer corrosion time, you can use a zinc phosphate plus this dry film, but we vapor hone most of these before we put the dry film on.

MR. SEYMOUR: Daniel Seymour, Air Force, Sacramento. How do you apply the coating? Brush?

MR. POCHILY: It can be applied through brush, dip, or spray. We at the arsenal are using electrostatic spraying. We find it is very efficient and it is very effective. We have cut consumption down about half.

Alternative Materials and Processes

Session IV

Wednesday Afternoon 3:45

ALTERNATIVES FOR CADMIUM METAL DEPOSITION IN THE FIELD OF MECHANICAL PLATING

Edward A. Davis
3M Company
Plating Systems Department
Saint Paul, Minnesota 55101

Methodology is not sufficiently ameliorated for total elimination of cadmium plating from some applications while sustaining its beneficial characteristics. However, by incorporating other metal powders with cadmium and depositing an alloy or co-deposit finish, inroads have been made which significantly reduce the consumption of cadmium and continue to maintain the integrity of the protective coating.

Two metal powders that have provided remarkable performance similarities to straight cadmium coatings when mixed with cadmium are tin and zinc. By removing half the amount of cadmium metal powder from a given mechanical plating procedure and replacing an equal amount of tin metal powder, a co-deposit coating is formed which meets and in some cases exceeds established specifications and test requirements. A 50% reduction in cadmium consumption is realized without any inhibiting or deteriorating product end use effects.

Zinc metal powder is employed in much the same manner. Successful results have been attained by further reducing the amount of the cadmium deposit. 75% zinc/25% cadmium combination coatings are curently being evaluated -- thus far, all results are positive. In many instances the cadmium/zinc combination coatings are receiving approved acceptance due to the following advantages:

1) Lower plating costs than straight cadmium or cadmium/tin combinations.
2) 75% reduction in the usage of cadmium.
3) Excellent corrosion protection.
4) Reliability of reproducing the finish.
5) Satisfactory torque tension drive characteristics.

Straight zinc, tin, and tin/zinc combinations do not satisfactorily replace all cadmium coatings because they fail to meet many specific corrosion requirements. These coatings, unless specially lubricated or waxed, also fail to qualify for various torque tension requirements called out in fastener drive specifications.

Preceding page blank

ALTERNATIVES FOR CADMIUM METAL DEPOSITION IN THE FIELD OF MECHANICAL PLATING

Submitted by

E. A. DAVIS
3M Company
23923 Research Drive
Farmington, Mich. 48024

ALTERNATIVES FOR CADMIUM METAL DEPOSITION IN THE FIELD OF MECHANICAL PLATING

Abstract

Metal finishing technology today has not as yet reached the point where industry can eliminate Cadmium and its reported negative features and still obtain Cadmium's beneficial finishing characteristics.

However, by incorporating other metal powders with Cadmium and depositing an alloy or co-deposit finish, the quantity of Cadmium in use has been reduced while the integrity of the protective coating itself is still maintained.

Two metal powders that have provided remarkable performance similarities to straight Cadmium coatings when mixed with Cadmium are Tin and Zinc. By removing half the amount of Cadmium metal powder from a given Mechanical Plating procedure and replacing it with an equal amount of Tin metal powder, a co-deposit coating is formed which meets, and in some cases exceeds, established specifications and test requirements. A 50% reduction in Cadmium consumption is realized without any inhibiting or deteriorating product end use effects.

Zinc metal powder is employed in much the same manner. Successful results have been attained by further reducing the amount of the Cadmium deposit. 75% Zinc/25% Cadmium combination coatings are currently being evaluated -- thus far, all results are positive. In many instances the Cadmium/Zinc combination coatings are receiving approved acceptance due to the following advantages:

1) Lower plating costs than straight Cadmium or Cadmium/Tin combinations.

2) 75% reduction in the usage of Cadmium.

3) Excellent corrosion protection.

4) Reliability of reproducing the finish.

5) Satisfactory torque tension drive characteristics.

Straight Zinc, Tin, and Tin/Zinc combinations do not satisfactorily replace all Cadmium coatings because they fail to meet many specific corrosion requirements. These coatings, unless specially lubricated or waxed, also fail to qualify for various torque/tension requirements called out in fastener drive specifications.

Preface

WHAT IS MECHANICAL PLATING?

Mechanical Plating is the cold welding of a ductile metal onto a metal substrate by the use of mechanical energy. The process is based on the fact that if an oxide free metal is placed in contact with another oxide free metal, metallic bonding can take place because of the free exchange of electrons.

Introduction

HOW DOES MECHANICAL PLATING WORK?

There are six basic items necessary to perform the process:

1) Multi-sided, lined barrel.
2) Metal powder.
3) Glass bead impact media.
4) Oil free parts.
5) Proprietary chemistry.
6) Room temperature water.

In the Mechanical Plating process, finely divided metal powder is charged into a multi-sided, lined barrel with glass bead impact media, oil free parts, proprietary chemistry, and a small amount of water. The barrel is rotated at various speeds dependent on part size and configuration. Rotational energy generated by the turning barrel is transferred to the parts through the sliding/tumbling action of the glass bead impact media. The proprietary chemistry produces and maintains oxide free surfaces of the substrate and also of the metal powder to be plated. The impact media ensures good contact between the metal powder and parts to be plated and facilitates plating of inner recesses of various part configurations. It is the glass bead media that actually peens the metal powder onto the substrate to form the sacrificial coating.

WHAT METAL POWDERS CAN BE PLATED BY THE PROCESS?

Typically, metals that are Mechanically Plated are ductile - the most common are Cadmium, Tin, and Zinc as well as various combinations of these powders. Other metals that have been Mechanically Plated are Lead, Indium, Silver, Copper, Brass and Tin/Lead solder. However, the demand for plating the last group of metal powders has not been large.

WHAT METALS CAN BE PROTECTED BY MECHANICAL PLATING?

Mechanical Plating is typically applied to a large and varied group of substrates including:

1) low carbon steel
2) cold rolled steel
3) high carbon heat-treated steel
4) various tool steels
5) high strength alloys
6) some stainless steels
7) free machining steels (including leaded steels)
8) nitrided steels
9) sintered iron (powder metallurgy)
10) some malleable iron and nodular iron
11) cast iron
12) copper
13) brass
14) bronze
15) lead
16) zinc diecastings

Mechanical Plating is a process for parts that are normally and typically batch handled, having no greater dimension than 6 in. (152.4 mm) in length and weighing less that 1/2 lb. (.227 kg) each. Significant strides have been made toward plating and handling of larger and heavier part types; however, the majority of parts currently being Mechanically Plated are of the smaller variety.

Plating Procedures

PROCESS STEPS:

1) Parts are thoroughly degreased and rinsed.

2) Parts and impact media are loaded into plating barrel.

3) Water level and temperature are adjusted to allow a small pool of room temperature water to appear just ahead of the tumbling load.

4) Barrel rotational speed is set.

PROCESS STEPS:

5) First surface conditioner for oxide, scale and rust removal is added.

6) Second surface conditioner is added for coppering step. *As previously discussed, many different types of substrates are coated. Various types of metal substrates will receive plating at different rates. By adding a copper strike, the metal powder does not see the substrate - only the copper - and the rate of deposition can be more closely controlled. Subsequent coating adhesion is also enhanced.*

7) Plating promoter is added. *This chemical is added to insure complete and even metal powder distribution to all surfaces within a given time cycle and to prevent lumpy or thin coatings (part to part variation).*

8) 'Flash' metal is added. *A small amount of metal powder (1 to 3 ounces per 100 sq. ft. or 28 to 85 grams per 9.3 sq. mtr. of surface area) is added to produce a thin coating completely covering each part. It has been determined that this 'flash' coating is beneficial in providing a tight, adherent bond between the substrate and the protective plating metal.*

9) Plating metal is added. *Plating metal is added in one or two increments depending on desired thickness and part configuration.*

10) Parts, media and spent plating chemicals are discharged. After discharge, the plater barrel is re-charged and the next load started. Parts and media are either screen or magnetically separated, and the media is rinsed and put in stand-by for the following run. The parts are post plate treated, dried, and packaged for shipment. Spent plating chemicals are pumped to a holding reservoir for subsequent waste treatment. Time sequence for a complete plating cycle runs between 40 and 55 minutes.

Advantages and Benefits

MECHANICAL PLATING PROVIDES:

1) Assured product reliability through elimination of hydrogen

MECHANICAL PLATING PROVIDES:

1) embrittlement. A published technical report titled "A Study of Hydrogen Embrittlement and Hydrogen Content of Hardened Steel Parts" is available upon request.

2) Mechanical cleaning action from the media which definitely aids in scale removal and shortens the time of the preplate cycle.

3) Ability to plate tangling and flat parts completely and evenly. The impact media tends to keep tangling parts and flat parts which normally mask from making contact with others, allowing complete plating deposition.

4) A system that consumes all chemistry during each process cycle eliminating bath maintenance.

5) Ability to change metal coatings from batch to batch in the same equipment.

6) Non-complex waste treatment procedures; no cyanides or chelating agents are used in the process.

7) Ability to plate powder metallurgy without impregnation. A technical bulletin titled "Mechanical Plating of Powder Metallurgy" has been published and is available upon request.

8) Attractive economics especially for coatings in the 0.0003" (0.0076mm) and higher range.

9) Good adhesion and uniformity of coating on interior and exterior of part.

10) Ability to deposit heavy coatings in the 0.002" to 0.003" (0.05 to 0.076mm) range. This process is called Mechanical Galvanizing and has application in many industries where heavier coatings are specified. The difference between Mechanical Plating and Mechanical Galvanizing is basic:

Mechanical Plating deposits a protective metal coating onto a substrate in a thickness range from 0.0001 to 0.0007 inch (0.00245 to 0.0177mm). Mechanical Galvanizing plates substrates in thickness ranges from 0.00075 to 0.003 inch (0.019 to 0.0762mm). The chemistry and procedure used for the Mechanical Galvanizing finish is similar to Mechanical Plating; however, plating cycle times are 15 to 30 minutes longer per run because metal powder deposits are up to 10 times heavier than normal coatings. The heavier deposits necessitate a longer cycle time to achieve complete plating consolidation. The advantages of Mechanical

PROCESS STEPS:

5) First surface conditioner for oxide, scale and rust removal is added.

6) Second surface conditioner is added for coppering step. *As previously discussed, many different types of substrates are coated. Various types of metal substrates will receive plating at different rates. By adding a copper strike, the metal powder does not see the substrate - only the copper - and the rate of deposition can be more closely controlled. Subsequent coating adhesion is also enhanced.*

7) Plating promoter is added. *This chemical is added to insure complete and even metal powder distribution to all surfaces within a given time cycle and to prevent lumpy or thin coatings (part to part variation).*

8) 'Flash' metal is added. *A small amount of metal powder (1 to 3 ounces per 100 sq. ft. or 28 to 85 grams per 9.3 sq. mtr. of surface area) is added to produce a thin coating completely covering each part. It has been determined that this 'flash' coating is beneficial in providing a tight, adherent bond between the substrate and the protective plating metal.*

9) Plating metal is added. *Plating metal is added in one or two increments depending on desired thickness and part configuration.*

10) Parts, media and spent plating chemicals are discharged. After discharge, the plater barrel is re-charged and the next load started. Parts and media are either screen or magnetically separated, and the media is rinsed and put in stand-by for the following run. The parts are post plate treated, dried, and packaged for shipment. Spent plating chemicals are pumped to a holding reservoir for subsequent waste treatment. Time sequence for a complete plating cycle runs between 40 and 55 minutes.

Advantages and Benefits

MECHANICAL PLATING PROVIDES:

1) Assured product reliability through elimination of hydrogen

MECHANICAL PLATING PROVIDES:

10) *Galvanizing follow closely those of Mechanical Plating; the merits of the Mechanical Galvanizing process are as follows:*

- A) Batch-to-batch and part-to-part uniformity.
- B) Simple and easy control of plating thickness.
- C) Freedom from hydrogen embrittlement.
- D) Room temperature process - no molten metal baths or noxious fumes.
- E) Elimination of 'stickers'. *In the molten metal/hot dip process, parts often stick together requiring (in some cases) 100 percent inspection after processing.*
- F) Simple waste treatment.
- G) No re-tap after plating. *In the molten-metal dip process, internal threaded components must either be plated and re-tapped to clean out thread roots, or plated as blanks and then thread tapped. Neither method provides corrosion protection for threaded areas. With the Mechanical Galvanizing process, normally over-tapped internal threaded components are plated per standard procedure. Plating protection is provided in all recessed areas, and there are no problems with ease of assembly or thread fit.*
- H) Low energy requirements/attractive economics.
- I) Ability to deposit multi-metal or alloy coatings for increased corrosion protection. *In salt spray testing the addition of 25 percent tin metal powder to the heavy zinc coating (0.021 in. or 0.053mm) provides up to 400 additional hours of corrosion protection.*
- J) Smoother and improved appearance over the molten metal dip coating application.

Users and Specifiers

Because Mechanical Plating is a unique process for applying corrosion-protective coatings, the list of its users is quite extensive. Primary users of the process are industries concerned with these factors:

1) Hydrogen embrittlement.
2) Alloy coatings.

3) Torque drive relationships.
4) Powder metallurgy.
5) Heavy Coatings.

The performance of Mechanical Plating in areas of corrosion protection can be specifically tailored to end-user requirements. Salt-spray data are available which details various finishes lasting from 24 to 20,000 hours of exposure time. The performance of Mechanical Plating in areas of torque drive relationships can also be tailored to meet specific requirements.

Results and Discussion

The Mechanical Plating process has the unique capability of producing multi-metal finishes by co-depositing a mixture of metal powders. Many factors must be put into perspective when selecting a finish for a given application. To meet end user needs, requirements, and demands in areas of product reliability, corrosion protection, torque drive relationships, and economics, a considerable amount of time and effort has been devoted to developing multiple metal coatings. Examples are the Cadmium/Tin coatings used widely throughout the Automotive and Marine industry. They were initially developed as alternatives to straight Cadmium coatings, and have several inherent and desirable characteristics. Straight Cadmium coatings, when given a post-plate chromate for increased corrosion protection, take on an iridescent or straw-colored appearance. However, Cadmium/Tin coatings, when given the same iridescent chromate treatment, remain silver-colored but take on the corrosion protection provided by the post-plate treatment. The Tin does not accept the iridescent color but the overall coating does exhibit increased corrosion protection. Results reveal a finish that has the corrosion protection equal to or better than straight Cadmium, that remains silver where brighter coatings are called for, has similar torque drive relationships to straight Cadmium, and is cheaper than straight Cadmium to produce. Market prices of metal powders fluctuate at a very uncertain and unpredictable rate. The cost of Mechanical Plating is directly attributable to the ups and downs of metal powder prices.

An additional and very important benefit is a 50 percent reduction in Cadmium consumption. While continuing to maintain the integrity of the protective finish the overall Cadmium usage has been significantly reduced, the end user does not suffer product deficiency, and the loss of Cadmium into the environment is minimized.

Cadmium/Zinc is yet another co-deposit coating that is proving very promising in the metal finishing field. This finish, still undergoing rigid testing, was primarily developed as a high performance coating for components that fasten dissimilar or bimetallic surfaces. The trenchant posture of this coating is the fact that up to 75 percent of Cadmium can be eliminated from a given procedure with no deterioration in end use affects.

Fasteners coated with the 75 percent Zinc/25 percent Cadmium combination coating, when tested in salt-spray environment against aluminum, far surpassed similar thickness coatings of straight Zinc, straight Cadmium, Cadmium/Tin, and Lead/Tin/Zinc combination coatings. The advantages of the Cadmium/Zinc combination coatings are as follows:

1) Up to a 75 percent reduction in the consumption or usage of Cadmium.

2) Lower plating costs than straight Cadmium or Cadmium/Tin combinations.

3) Excellent corrosion protection.

4) Reliability of reproducing the finish.

5) Satisfactory torque tension drive characteristics.

Mechanically Plated Cadmium/Zinc coatings in the 0.00025 in. (0.0063mm) thickness range (in contact with plain aluminum) have been tested for 1500 hours in salt spray environment without red rust corrosion damage to the fasteners or exfoliation corrosion damage to the aluminum. All initial testing was done in a 5 percent neutral salt spray cabinet (ASTM B117); now, outdoor exposure testing is underway along with actual road testing in assembled applications. Plating costs to produce the Cadmium/Zinc coatings are somewhat less than straight Cadmium or Cadmium/Tin coatings. Material costs only for the three finishes are as follows:

Cadmium/Tin	Straight Cadmium	Cadmium/Zinc
$12.58/100 lbs. (45.3kg)	$12.56/100 lbs. (45.3kg)	$6.27/100 lbs. (45.3kg)

Costs figured for U-Clip fasteners at 64 lbs./cubic foot (28.99kg/0.028cu.m) volume with a surface area of 150 sq.ft./100 lbs.(13.95 sq.m./45.3kg).

Summary

Mechanical Plating utilizes mechanical energy to provide parts that can be batch-handled with various protective finishes. The part types, along with selected glass bead impact media and finely divided metal powder, are barrel-tumbled in a chemically controlled aqueous environment. The metal powder added is cold-welded to the part types which provides the parts with an adherent, sacrificially protective metallic coating.

Mechanical Plating has the unique capability of enabling deposition of multiple metals without inherent process deterrents. It is currently being utilized in replacement of a percentage of Cadmium by alternative metals having their own special advantages. This enables retention of the Cadmium characteristics which have proven advantageous while at the same time reducing the total amount of Cadmium consumed for any given quantity of parts plated.

Mechanical Plating provides the end-user with product reliability, freedom from hydrogen embrittlement, consistent corrosion protection, uniform controlled coatings, proper torque drive relationships, tailor-made coatings for specific corrosion and bimetallic fastening situations, and competitive economics.

Alternatives for Cadmium Metal Deposition in the Field of Mechanical Plating

MR. ISLER: William Isler, Harry Diamond Laboratories. Has this technique been applied to coating insulators; for example, if you were trying to provide an RF shield to a circuit that has been encapsulated, say, in epoxy. Will it stick to an insulator? Do you have to coat one metal onto another metal for this process?

MR. DAVIS: We don't put deposition onto a plastic or a resin. The process is for steel or metal.

MR. GORDON: Philip Gordon, Cutler-Hammer. After you have applied your coating, if you make a metallographic cross-section, do you see a copper layer and a metal strike layer and then your final metal built-up layer?

MR. DAVIS: You can definitely see the copper layer in a microsection.

MR. BOOKER: Jonathan Booker, Brush Wellman. How do you avoid incorporating the glass bead impact media into the coating?

Do you see any glass in there?

MR. DAVIS: We have on the plating of heavier part types. I didn't get into any of the disadvantages of mechanical plating. In the plating of very heavy part types, we sometimes pulverize the glass beads and then some of the pulverized glass is included in the coating.

We have run torque drive relationship with these coatings and also salt spray to see if the effect of the powdered glass in the coating would be damaging. We really haven't found it damaging.

There are two other disadvantages. One is that we cannot apply a very finite micro-inch finish, and we don't have a finish that has a high luster. That is because we are peening down a metal powder and then another metal powder on top of it. As a result, we have a matte finish or an orange peel effect.

The third disadvantage we find is that we cannot handle all the larger part types that we are asked to plate. A case in point is when one of the highway commissions asked us if we could plate bars in 18 to 42 foot lengths. We don't have a barrel big enough to tumble those.

MR. KANN: Sam Kann, TRW. Are the coatings conductive and are they solderable?

MR. DAVIS: We do have some conductive coatings. With an acid flux, we can get solderability on some of the tin coatings. However, acid flux is a no-no in some electrical applications.

MR. KANN: Is the tin cast, 50:50, an electrically conductive coating for galvanic action against dissimilar metals such as copper, aluminum, or steel?

MR. DAVIS: We don't have a process at this point to plate onto aluminum.

MR. KANN: Suppose it were a steel screw that went onto a threaded brass nut in a salt spray application or a marine atmosphere.

MR. DAVIS: In the marine atmosphere, the tin-Cd coatings work very well in conjunction against brass or copper. We have several specifications written for that, so the answer to your question is yes.

MR. WHITE: Marty White, Cadmium Association. When you are talking about recesses or the inside of tubes, you are saying that you can plate as long as the glass beads can get inside. Surely the requirement is that you get inside and move rather than just get inside.

MR. DAVIS: Yes.

MR. WHITE: You wouldn't get a plate like that in the tip of a cone, for example?

MR. DAVIS: Yes. The right copper part to media ratio in the tumbling barrel must be used. If we have two volumes of media and one volume of parts, the media can hold the metal powder away from the parts. If you get the right mixture of media to the parts, we flow in and out of the recess area, and that facilitates the plating.

MR. WHITE: Do you have a range of glass bead sizes?

MR. DAVIS: We have ten different sizes ranging from six thousandths all the way up to 250 thousandths.

MR. HANNA: Ed Hanna, Red River Army Depot. When you were talking about degreasing, you did not say anything about solvent degreasing.

MR. DAVIS: I didn't bring that up because we don't like vapor degreasing unless the vapor degreaser is kept very clean. The blanket of vapor that forms over the parts will hold oil particles in suspension, and when the parts are brought out of the vapor degreaser, the oil redeposits itself on the surface. It doesn't take very much oil to coat each little four-micron zinc particle and not allow it to go on the surface with good deposition. So we tend to stay away from vapor degreasing wherever possible.

MR. HANNA: What if the part has been blast-cleaned or painted before plating?

MR. DAVIS: There is no problem in doing that. In fact, that gets done on a daily basis.

Alternative Materials and Processes

Session IV

Wednesday Afternoon 4:20

STATE OF THE ART FOR HIGH RATE SPUTTER DEPOSITION

J. W. Patten
E.D. McClanahan, R.A. Busch, R.W. Moss,
M.A. Bayne and E. N. Greenwell
Battelle
Pacific Northwest Laboratories
Materials & Process Engineering Section
Richland, Washington 99352

A brief description of the principles of the sputtering process and of advanced sputtering systems is provided along with a description of a typical experimental procedure referenced to one of these advanced systems. Features of this technology include the ability to deposit high integrity materials and complex alloys at rates of 1 to 10 mils thickness per hour for use as coatings or free standing hardware. The coatings are typically free of growth defects. Further, metallic materials may be deposited on areas of several square feet to a thickness uniformity of ± 10%. Ceramic materials may be deposited at rates on the order of 1 mil thickness per hour. Free standing parts may also be produced from unique combinations of materials to obtain lamellar composites and precipitation and dispersion hardened alloys. Compositions may be graded over a range of deposit thickness to obtain coating-substrate material combinations normally impossible to achieve because of debonding via thermal expansion or chemical incompatibilities. Deposit-substrate bond strengths at least equal to the strength of the lowest strength material of the pair are to be expected. Examples of material and deposit geometries to which this technology have been applied are discussed.

STATE OF THE ART FOR HIGH RATE SPUTTER DEPOSITION

E.D. McClanahan, R.W. Moss, N. Laegreid, J.W. Patten,
R.A. Busch, M. A. Bayne, E.N. Greenwell

Materials and Process Engineering
Battelle Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington 99352

Abstract

A brief description of the sputtering process and of advanced sputtering systems is provided along with a description of a typical experimental procedure referenced to one of these advanced systems. These systems are able to deposit metals and alloys at rates of 1 to 10 mils thickness per hour for use in coatings or free standing hardware. The metallic coatings are typically free of growth defects, and may be deposited on areas of several square feet while maintaining a thickness uniformity of ± 10%. Ceramic materials may be deposited at rates on the order of 1 mil thickness per hour. Free standing parts may also be produced by combining materials to obtain lamellar composites and precipitation and dispersion hardened alloys. Compositions may be graded over a range of deposit thicknesses to obtain coating-substrate material combinations normally impossible to achieve because of debonding via thermal expansion or chemical incompatibilities. Deposit-substrate bond strengths at least equal to the strength of the lowest strength material of the pair are to be expected. Examples of material and deposit geometries to which this technology have been applied are discussed.

Introduction

This paper describes the sputter deposition process in general and some of the characteristics of the high rate sputter deposition techniques and equipment currently used at Battelle-Northwest Laboratories (BNW). The objective of this discussion is to identify high rate sputter deposition as an alternative to other coating techniques and to indicate unique coating capabilities and coating material properties that could be beneficial in specific applications. Of immediate interest to this conference is the observation that, in general, sputtering would not be considered as a reasonable alternative to conventional cadmium plating because of its comparatively high cost and the large volume throughput which many cadmium plating applications require. However, the emergence of more sophisticated treatment processes, the great reduction in the use of cadmium which may be imposed in the future to reduce cadmium contamination of the environment, and the high intrinsic value of many parts requiring a coating means that each application or proposed application of the present cadmium electroplating process must be reviewed individually to determine the suitability of other coating materials and/or coating processes. High rate sputter deposition technology can provide high quality coatings of many different materials with a wide range of properties on almost any substrate so that consideration of this technology should be included in any extensive review of a critical coating requirement. After a brief discussion of the sputtering process itself, and aspects of an advanced sputter deposition technique, some of the unique properties of sputtered materials will be discussed, along with some of the applications to which high rate sputtering has been applied. Some observations have been made in the literature and are general to most sputter deposition laboratories. Others, which will be noted, are particular to Battelle-Northwest and have not been widely discussed.

Discussion of the Sputtering Process

1. The Sputtering Phenomena

Evidence indicates that sputtering is a momentum transfer process.(1,2) A simple model illustrating momentum transfer through binary collisions is shown in Fig. 1. Positively-charged ions are accelerated to the surface of the target, which provides the material for coating. Sufficient energy can thus be transferred to the target atoms to overcome their binding energy in the lattice. The impact of a single ion on the target can cause the ejection or "sputtering" of many target atoms. The ratio of ejected atoms to incident ions is called the sputtering yield. Sputtering yields are dependent on the binding energy of atoms in the target and the mass and energy of the bombarding ions.

2. Principle of Operation of a Triode Sputtering System

The use of sputtering as a practical deposition process depends on achieving a large current of high energy ions at the surface of a target of the desired geometry and coating material. As illustrated in Fig. 2, this may be done by immersing the target in a dense plasma generated between a thermionic cathode and an anode in an evacuable chamber containing inert gas. The ions are formed by collisions between electrons and inert gas atoms, and are accelerated into the target surface by a large negative applied voltage. The sputtered target atoms leave the surface with approximately a cosine spatial distribution. By properly designing the target/substrate and shield geometrical relationship,(3) a uniform thickness distribution may be obtained. This is accomplished with sputtering chamber hardware, Fig. 3, that has been designed with the built in flexibility to accommodate a variety of target/substrate configurations, without extensive modifications. In most cases, one configuration can be removed and replaced with another in a matter of minutes. To eliminate pinhole type defects and other growth defects, BNW uses special arc suppressing circuitry. Computerized process control techniques enhance deposition-to-deposition repeatibility, required for production applications. To insure deposit quality, a residual gas analysis system is used to continuously monitor the sputtering chamber atmosphere during deposition.

In theory, any material with a reasonably low vapor pressure may be sputtered. Therefore, in theory, great freedom exists to apply sputtering to the formation of both existing and new materials with unique properties. This freedom has been exercised at BNW to form coatings not obtainable in other ways for over ten years. Special material property effects for a particular application are obtained by varying the composition of the target material; varying deposition parameters, such as electrode voltages and current densities; varying substrate temperature and surface condition; and by altering the geometrical configuration of the sputtering system itself. The measurement and evaluation of resultant coating properties provides information permitting accurate prediction of the results of future depositions. Enhancing this iterative process is the computer logging of data and computer control over selected parameters which insures deposition-to-deposition reproducibility. Over 40 variables are continuously monitored during sputtering by computer programs especially developed for this purpose. In the case of deposit thickness, for example, thickness measurements from initial deposition provide data permitting selection of deposition parameters necessary to obtain a specific coating thickness.

3. Typical Deposition Procedure

Complex shapes may be deposited in existing apparatus similar to the one depicted,Fig. 4. The apparatus is enclosed in a water-cooled stainless steel vacuum chamber which is evacuated by a liquid nitrogen trapped oil diffusion pump to base pressures of about 10^{-7} Torr without baking. The power supplies for the discharge current, sputtering target, and substrate etching or bias, are equipped with current limiting and cutback circuits which limit overcurrents during arcs and reduce the power supply output to zero within 5-10 μ sec. The target to substrate spacing is nominally 1-1½ inches and the target is up to 9 in. in diameter and water cooled on the back surface. Substrates could be any device up to 6 in. long and 5 in. major diameter. All surfaces upon which a coating is desired must have line of sight to some portion of the target for some portion of the deposition. This eliminates sharply convoluted surfaces and holes with small aspect ratios from being coated in this apparatus. Depending upon the desired result, the substrate may be water-cooled (15-25°C), air-cooled (≈300°C) or heated (up to 1000°). Each type of substrate has its own procedure for cleaning prior to deposition.

Prior to assembly of the apparatus, all internal surfaces are vapor degreased and ultrasonically cleaned. After assembly, the system is evacuated and helium leak checked. At this time the electrical resistance of each electrode is also checked to eliminate the possibility of internal short circuits. After a four hour (minimum) pumpdown, the outgassing rate of the system is measured and if satisfactory, a dynamic atmosphere of krypton is established at a pressure of about .003 Torr. Then a termionic discharge is ignited between the cathode and anode, and increased in power over a 15-30 minute period. The substrate is then ion etched, typically for 5-10 minutes at -100 volts, 5 ma/cm^2 ion current density. Finally the target power is increased over an additional 15-60 minute period to typical values of 1500-2500 volts and 5-20 ma/cm^2. This power ramping produces smoother (i.e. fewer arcs) depositions.

Target power is maintained until the desired coating thickness is obtained on the substrate. After the deposition a cooldown period is required prior to disassembly if some electrodes, or the substrate are designed to be hot during the deposition. Post-deposition heat treating or final machining may be required for some types of coatings but many are ready for immediate use upon removal from the sputtering chamber.

Technological Capabilities and Application Examples

To obtain an advanced technological position in high rate sputtering, one must possess certain capabilities. Some of these capabilities are identified and examples using the capability are presented. References for these examples and other work performed at BNW are listed in the appendix.

- Deposit theoretically dense, high integrity metals and complex alloys at rates of 1- to 10-mils thickness per hour (depending on material) for use as coatings or free-standing hardware. Sputtered deposits have been made on a wide variety of substrate geometries such as flat plates (Fig. 5), inside surfaces of cylinders (Fig. 6, 7), and complex shapes with both concave and convex areas (Fig. 8, 9, 10). Deposits with thicknesses ranging up to ∼ 1/2 inch and weighing up to 12 pounds have also been made (Fig. 11).
- Deposit metallic materials on areas of several square feet to a thickness uniformity of ± 10% at rates of mils per hour. In specific applications, where required, thickness uniformities down to ± 2% are obtainable (Fig. 12, 13).

- Expand sputtering process capability in terms of deposition rate, object size, production rate, etc. This ability to scale-up a laboratory process to a full production system was a key factor in the development and transfer of technology to Rockwell International Company (Rocky Flats Plant) of the first production application of semiautomated high-rate sputtering. With this background, and the continuing development of sputtering technology at Battelle-Northwest, our ability to develop and demonstrate production prototype sputter-deposition equipment with subsequent transfer of technology to industry for production is well established.
- Form "bulk" and/or free-standing parts from unique combinations of materials to obtain lamellar (layered) composites, and precipitation and dispersion hardened alloys, (Fig. 14, 15, 16, 17, 18).
- Grade in composition and/or properties over a range of deposit thickness to obtain coating-substrate material combinations normally impossible to achieve because of debonding via thermal expansion or chemical incompatibilities, (Fig. 19, 20). This technique may also be used with free-standing materials.
- Obtain deposit-substrate bond strengths at least equal to the strength of the lowest strength member of the pair. In most cases fracture during testing does not occur at the bond but in the lowest strength member, (Fig. 21).
- Deposit ceramic materials at rates on the order of 1-mil thickness per hour.
- Control the structure and composition of semiconductor and insulator films and tailor their electrical and optical properties for specific applications.
- Control the incorporation of sputtering gas into the deposit from <1 appm to $>10^4$ appm.

Properties of Sputtered Deposits

A wide variety of materials, including most pure metals amenable to sputtering and a number of commercially available alloys, have been sputter-deposited under various contracts at Battelle-Northwest, Table 1. Selected properties of these materials which may be influenced by the sputtering process are discussed below.

- Oxidation Resistance - Our studies of the effect of sputter-deposition on the elevated temperature oxidation resistance of iron-base and nickel-base alloys have shown that sputter-deposited alloys can be made significantly more oxidation resistant than non-sputtered material of the same composition. This is illustrated, Figure 22, for AISI Type 304 stainless steel oxidized in air at 1200°C for 16 hours. The oxidation rate for the sputtered stainless steel was less than a tenth the rate for the wrought control material. Furthermore, the oxide layer that formed on the sputter-deposit was more adherent and had a higher chromium content than the oxide layer on the non-sputtered stainless steel of the same composition. A similar improvement in oxidation resistance is illustrated for 304 stainless steel deposited at 700°C on a substrate of wrought 304 stainless steel and oxidized in air at 1000°C for 60 hours. In both cases the sputtered stainless steel retained the fine-grain size characteristic of as-deposited material even after long-term testing at elevated temperatures.

In an extension of this work, the oxidation resistance of Ni-20 Cr alloy was increased significantly by producing sputter-deposits containing 5 vol% alumina to stabilize the fine-grained, as-deposited material. The average oxidation rate for the sputtered alloy was one-fourth the rate for the non-sputtered control material after 1000 hours at 1100, Fig.23.

These results demonstrate that sputter-deposition can be used to produce alloys with a high degree of microstructural stability and with significantly improved resistance to high-temperature oxidation. One application of these findings would be to use sputter-deposition to coat high-temperature alloys with material of essentially the same composition to minimize normal coating incompatibility and interdiffusion problems while providing the enhanced oxidation resistance required for long-term, elevated-temperature service.

- Corrosion Resistance - A major problem in adapting gas turbine engines for marine use is the hot-section materials used in the aircraft engine are susceptible to sulfidation corrosion. The hot corrosion and sulfidation resistance of marine gas turbine blades and vanes has been improved markedly through the use of sputter-deposited platinum and cobalt-chromium-aluminum-yttrium(CoCrAlY) alloy coatings. Platinum may be deposited on production physical-vapor-deposited (PVD) CoCrAlY coatings, Figure 24, to increase the production coatings hot-corrosion resistance. It is believed the Pt retains Al near the free surface by forming stable Pt-Al compounds, Figure 25. During service, these compounds release Al to form oxides and provide increased corrosion resistance.

In addition to improving the present PVD production coating with the platinum, sputter-deposition offers a means of improving the CoCrAlY coating itself. Sputtered CoCrAly has been deposited over a production PVD coating and representative metatography of one blade is given in Figure 26. The sputtered CoCrAlY consists of two layers with different

Al contents. These were obtained by using different voltages on the aluminum target, Fig. 4. This metallagraphy shows the high integrity, leader-free, fine-grained microstructure that can be obtained. The improvement in performance of the sputtered coating was proven during at-sea tests and may be attributed to the improved microstructure, which severely limits the sites available for base-metal attack.

- Mechanical Strength - Copper, with its high thermal conductivity was an essential construction material for a special pressure vessel, but it lacked the required mechanical strength. Fig. 27 shows the effects of small additions of alloying elements to form dispersion hardened alloys and the effects of deposition temperature on the tensile strength of the material. This program allowed the selection of a material with the required mechanical strength without significantly reducing the thermal conductivity of the copper.
- Electrical Resistivity - Figure 28 shows the influence of substrate temperature during deposition on the resistivity of sputter-deposited CdS. The resistivity can be controllably varied over eight orders of magnitude by depositing at selected substrate temperatures between 20 and 300°C. Thus, for example, the low-resistivity CdS required for use in photovoltaic devices ($\simeq 10\Omega\cdot\text{cm}$) can be easily obtained by depositing at substrate temperatures near 70°C. The variation of the resistivity is due to a slight deviation from stoichiometry, always in the direction of excess Cd, which occurs at the lower substrate temperatures. The deposits made near 300°C are very nearly stoichiometric. Those made near room temperature contain an excess of Cd, or a deficiency of S, of $\sim$0.1 at %. The substrate temperature controls the sticking coefficient of the highly volatile sulfur, which re-evaporates from the substrate unless it reacts quickly with Cd to form the compound.

Summary

Because of restraints which may be imposed on the cadmium plating industry, alternatives must be sought which mitigate the adverse impact of cadmium on the environment. High rate sputter deposition is a viable alternative coating process if the restraints become very severe or the parts to be coated have high intrinsic value. Sputtering is a momentum transfer process that requires a clean vacuum environment and fairly stringent deposition procedures. Wide ranges in structural, chemical and physical properties may be obtained by varying deposition parameters and coating material. As examples, the improved oxidation resistance of sputtered stainless steel, the improved adhesion and sulfidation resistance of sputtered CoCrAlY, the improved strength of sputtered, dispersion hardened copper and the controlability of the resistivity of sputtered CdS were discussed. Some other features of high rate sputtering that are also important to consider are the high rate (1-10 mils/hour) deposition of theoretically dense adherent material, the ability to scale-up to production size, and the versatility in coating material selection that the sputtering process allows.

References

1. Wright, A.K., American Journal Science Arts, 13, 49 (1877)

2. Hyman, P., "Ionic Bombardment Theory and Application," J.J. Trillot, ed., Gordon and Breach, New York, 1964.

3. Moss, RW, McClanahan, E.D. Laegreid, N. US Patent 9,038,171, July 26, 1977.

TABLE I. Materials Deposited by High-Rate Sputtering

Extended Solubility in Eutectic and Immiscible Systems
Silver - cobalt, copper, nickel
Copper - tantalum

Dispersion Hardened Systems
Aluminum - beryllium, silicon
Copper - alumina, silicon carbide, tantalum carbide
Cobalt - titanium carbide
Titanium - yttria, tungsten
Nichrome - alumina
Iron chrome cobalt - alumina, thoria

Graded Composition Layers
Ni - ZrO_2
Ni, Cr - ZrO_2

Semiconductors
Cadmium sulfide
Cadmium telluride
Indium tin oxide
Silicon
Hydrogenated (amorphous) silicon

Nonequilibrium Phases
Beryllium - nickel
Boron - silicon

Compounds
Rare earth - cobalt magnets
Niobium-tin and niobium-aluminum-germanium superconductors
Alumina, yttria, zirconia, titania, silica

Pure Metals and Conventional Alloys
Unique properties and behavior

Protective Coatings
Platinum, CoCrAlY and zirconia for turbine blades
Chromium and tungsten for small arm receivers and barrels
Chromium, titanium and niobium for fissile oxide fuel pellets
Copper and silver to minimize laser absorption
Nickel, vanadium and titanium for titanium alloy corrosion
Titanium and tungsten carbides for wear of sintered tool bits
Titanium for mechanical protection and bonding of Al_2O_3 fibers
Copper and aluminum for light and x-ray telescope optics

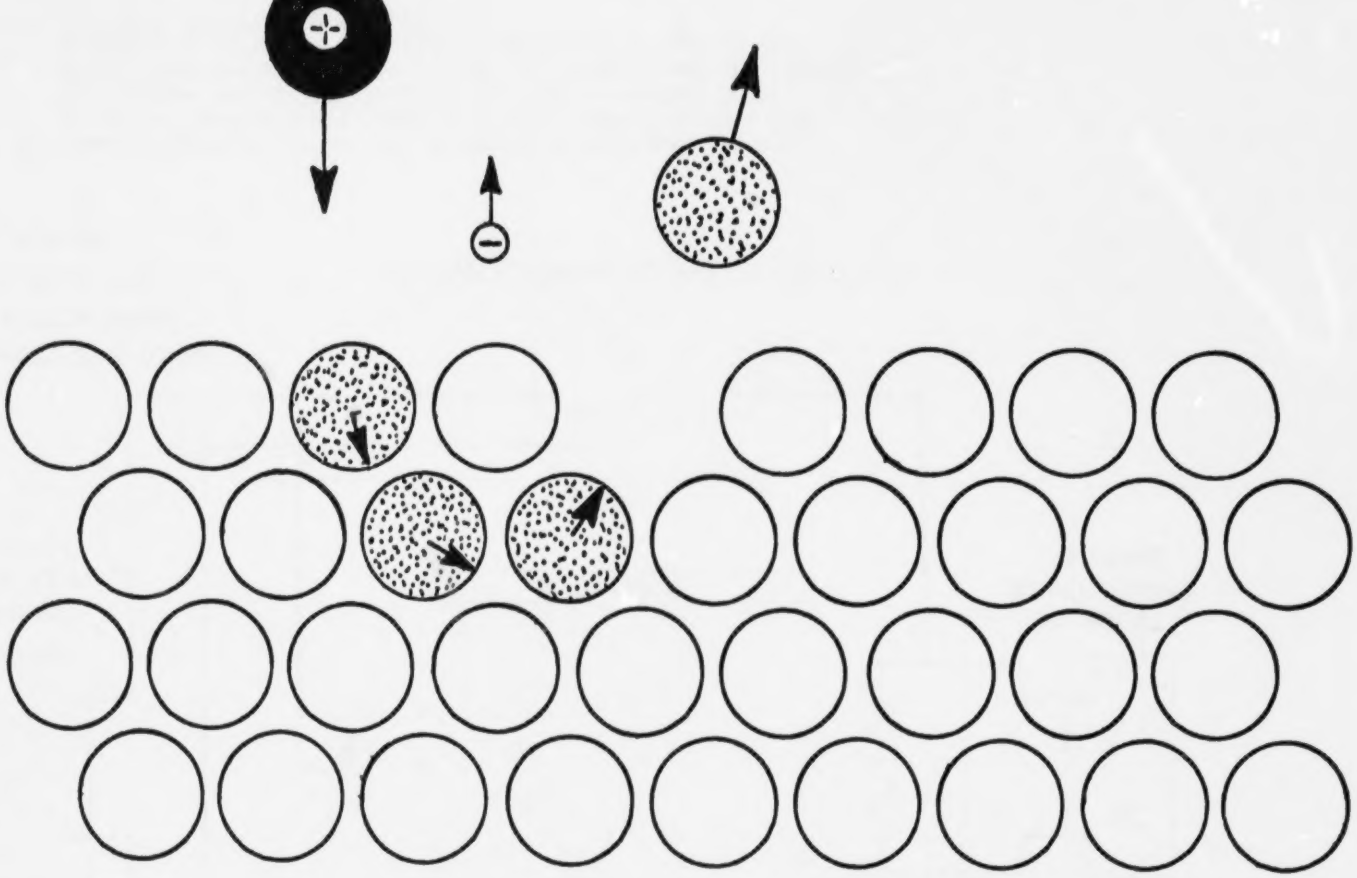


FIGURE 1. Basic Sputtering Mechanism. Ions of inert gases like argon, krypton or xenon strike the surface of the target, transferring momentum to the target atoms. When the target atom has enough velocity to overcome its binding energy it leaves the surface of the target.

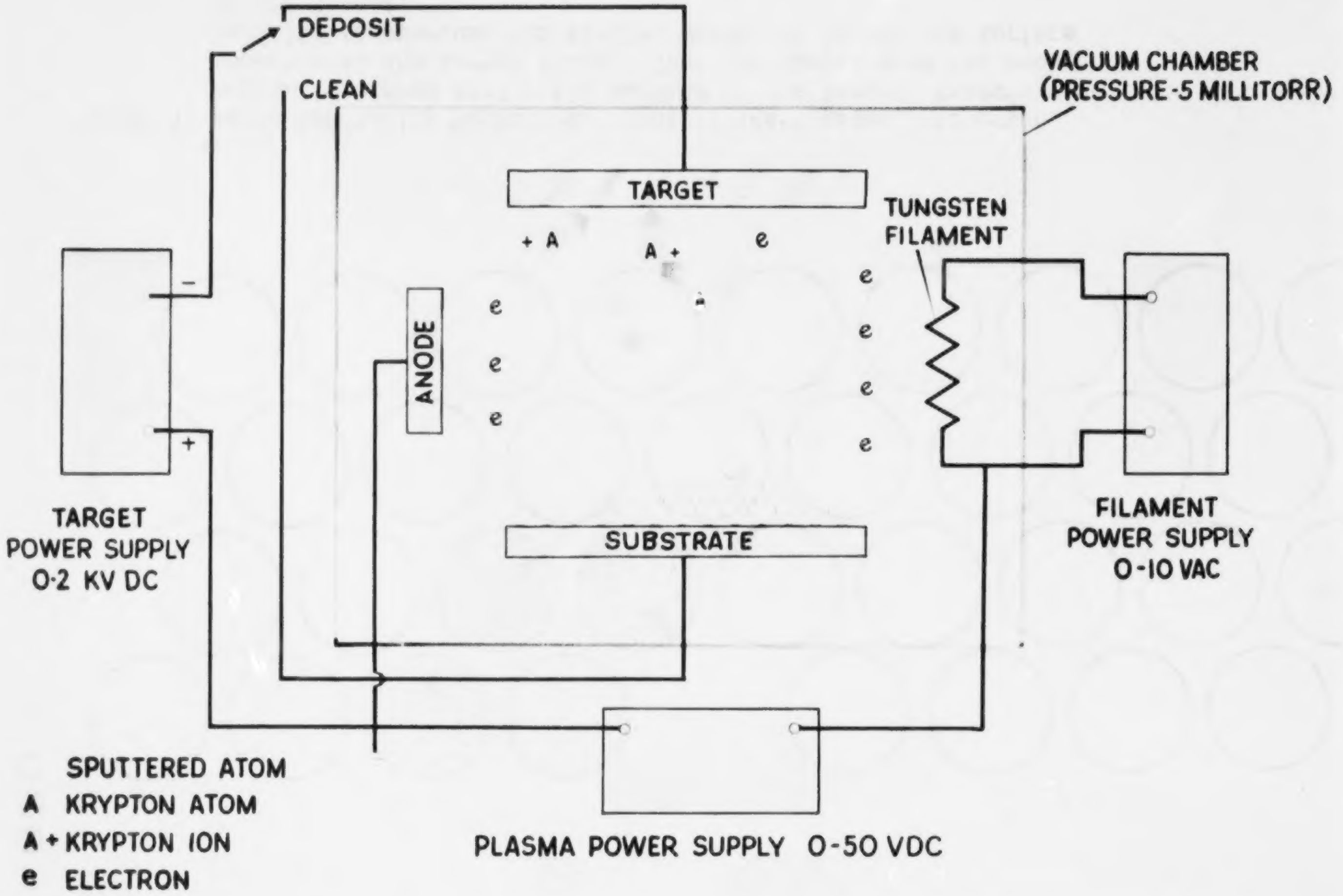

DEPOSIT
CLEAN
VACUUM CHAMBER (PRESSURE-5 MILLITORR)
TARGET
TUNGSTEN FILAMENT
+ A
A +
e
ANODE
SUBSTRATE
−
+
TARGET POWER SUPPLY 0-2 KV DC
FILAMENT POWER SUPPLY 0-10 VAC
PLASMA POWER SUPPLY 0-50 VDC
SPUTTERED ATOM
A KRYPTON ATOM
A+ KRYPTON ION
e ELECTRON

FIGURE 2. Triode Sputtering Components. A plasma of electrons and ions is created between a hot tungsten filament and an anode. When the negative voltage of electrons and ions is applied to the target, ions are accelerated towards it. These cause the ejection (sputtering) of target atoms, which subsequently land on the substrate, building up as a deposit.

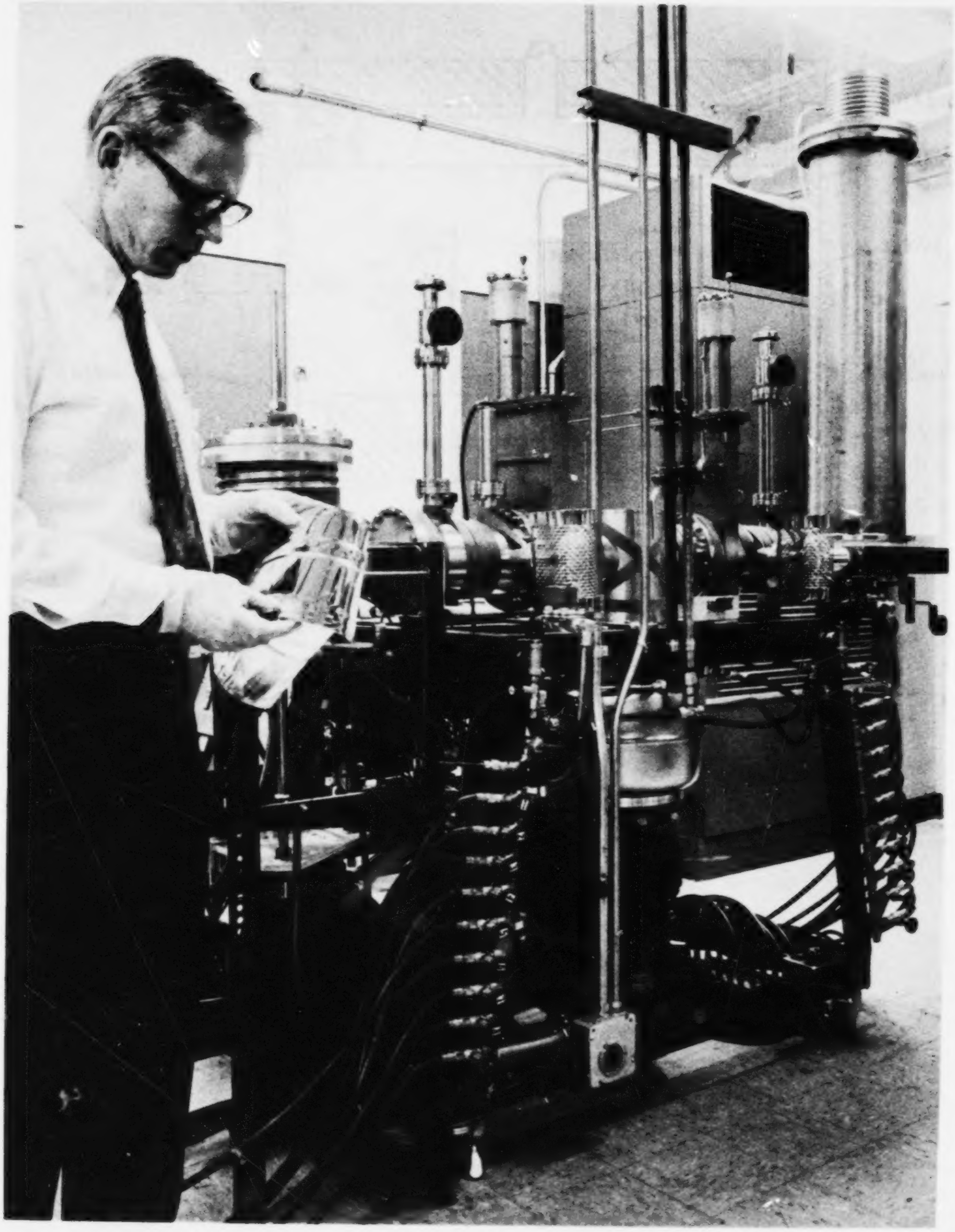


FIGURE 3. BNW Dual-Head Sputtering Apparatus. While a deposition is being performed on one end, the other is being prepared. Note the oil diffusion pump, cold trap, dual gate valves, ports for an RGA and cooling water manifold. The deposit being held is copper foil whose substrate was a pyrex pipe.

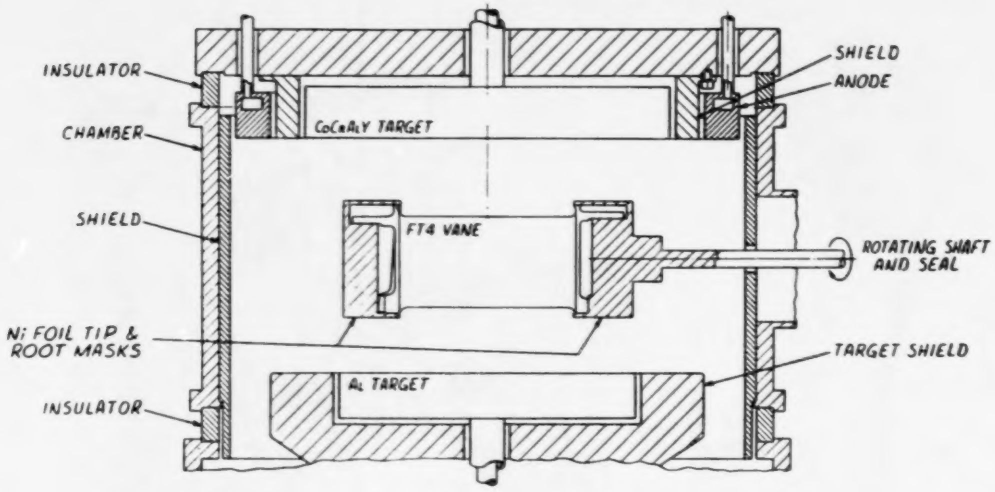


FIGURE 4. Representative High-Rate Sputtering Apparatus for Complex Substrate Shapes. This example shows a marine gas turbine vane in position to be coated with CoCrAlY that may be made rich in aluminum with a supplementary target. The hot tungsten filament is not shown.

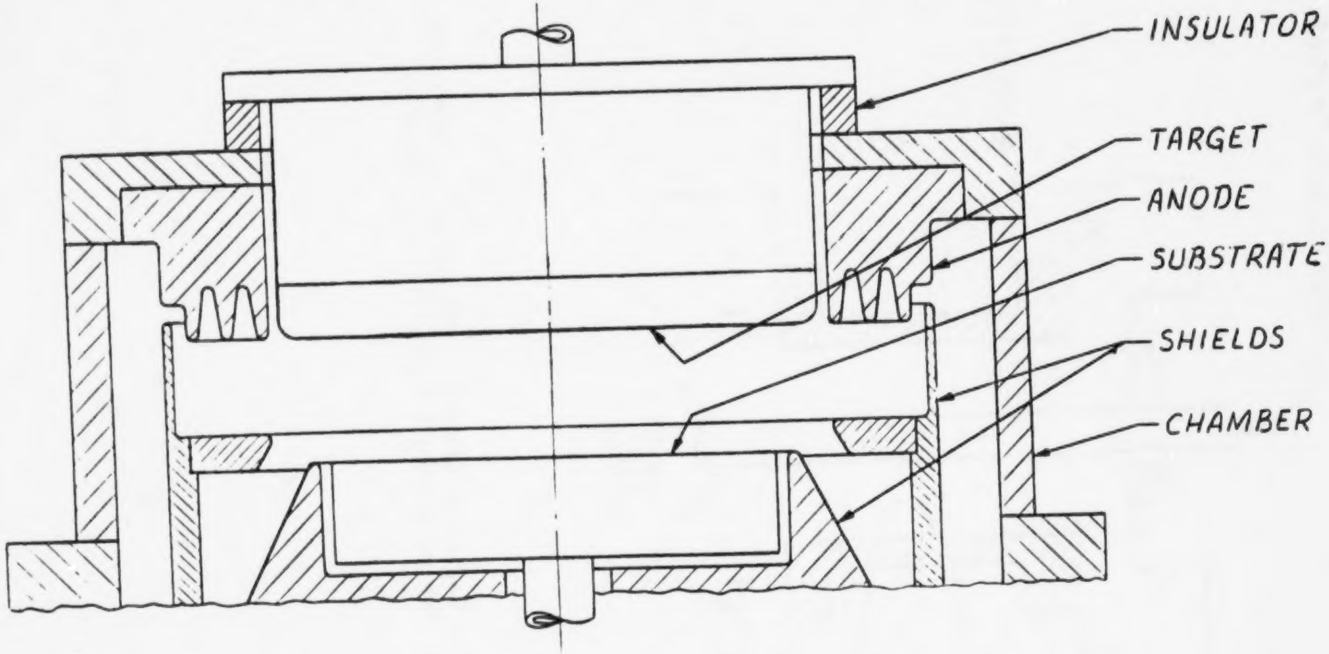


FIGURE 5. Flat-Plate Target-Substrate Sputtering Geometry. The substrate generally has a smaller diameter than the target in this mode to give a better thickness distribution at the substrate because the target atoms are ejected with approximately a cosine spatial distribution.

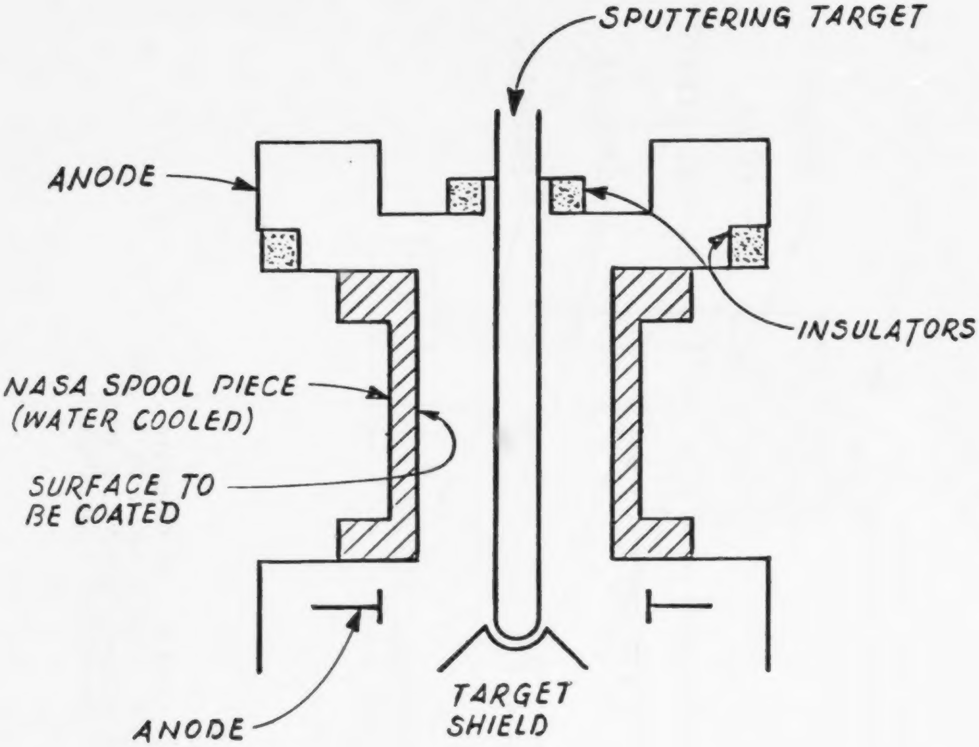


FIGURE 6. Coaxial Cylinders Sputtering Geometry. The target is longer than the substrate to improve the deposit thickness distribution.

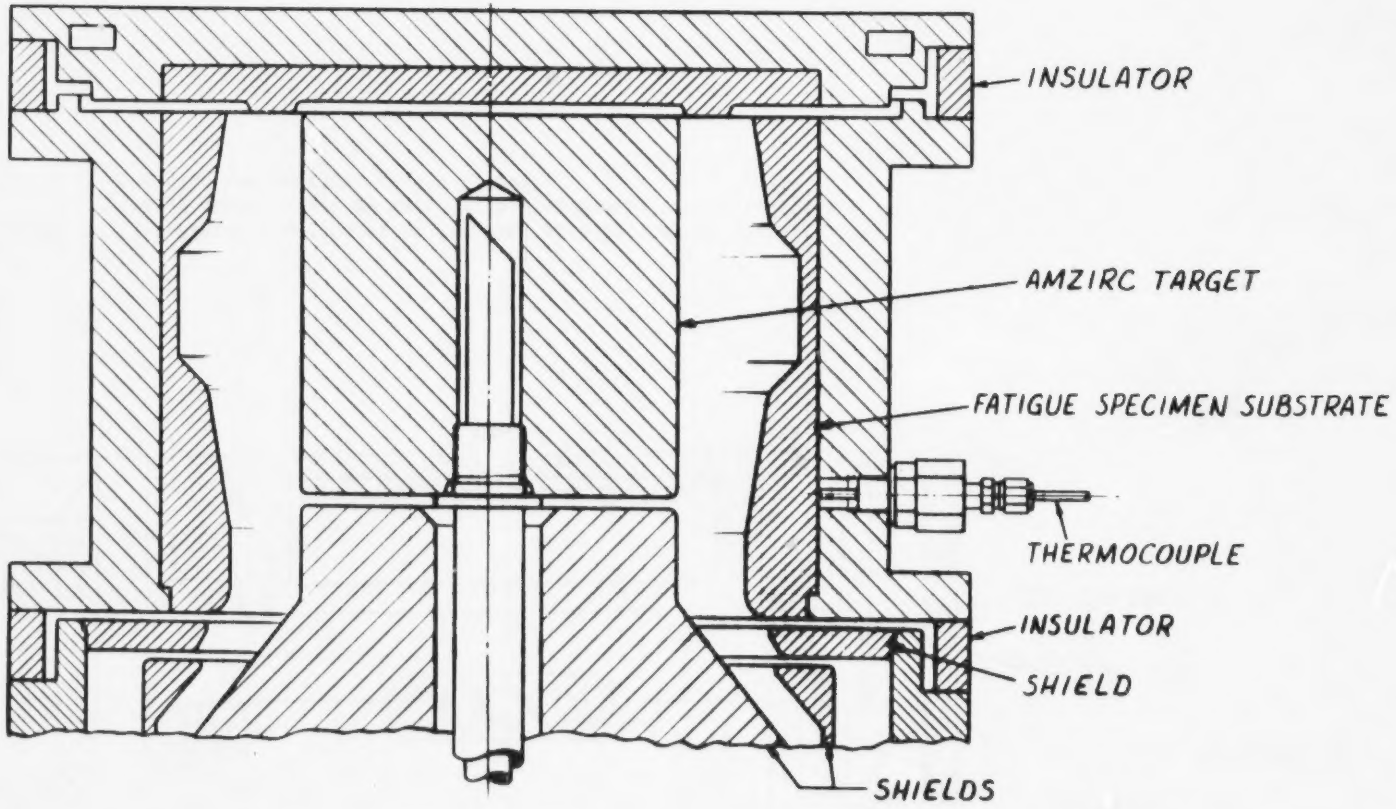


FIGURE 7. Coaxial Cylinders Sputtering Geometry. The target may be designed to yield a specific thickness distribution.

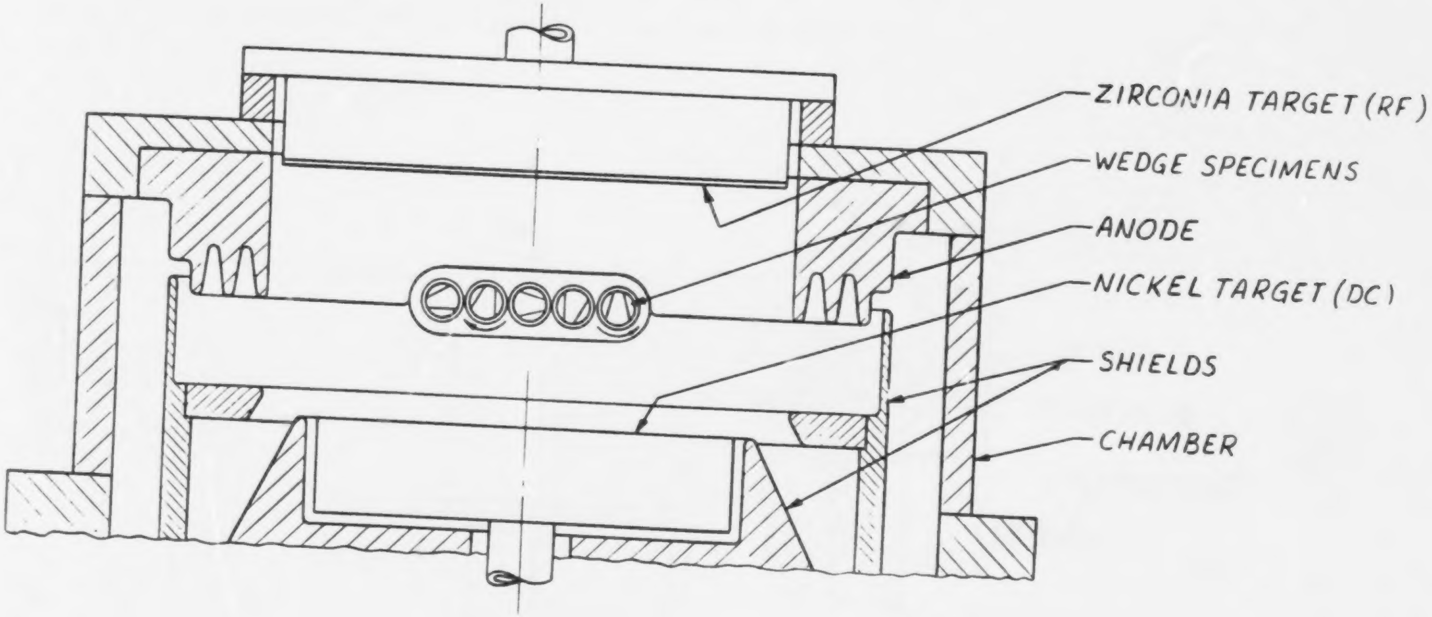


FIGURE 8. Flat-Plate Target-Rotating Pin Substrate Sputtering Geometry. Graded deposits may be made in this apparatus by continuously changing the voltages on the targets.

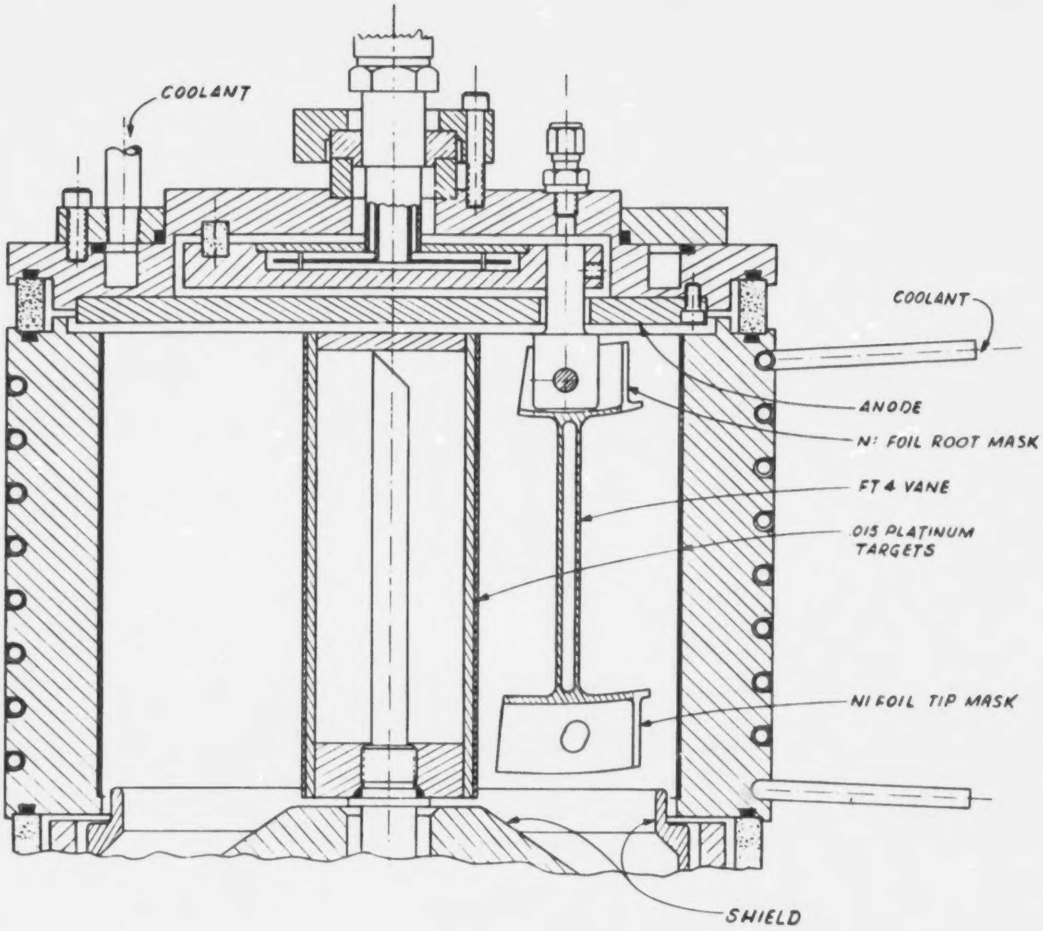


FIGURE 9. Concentric Cylindrical Targets for Complex Substrate Shapes. This apparatus has a high throughput and is used primarily for depositing thin layers that must be heat treated prior to use.

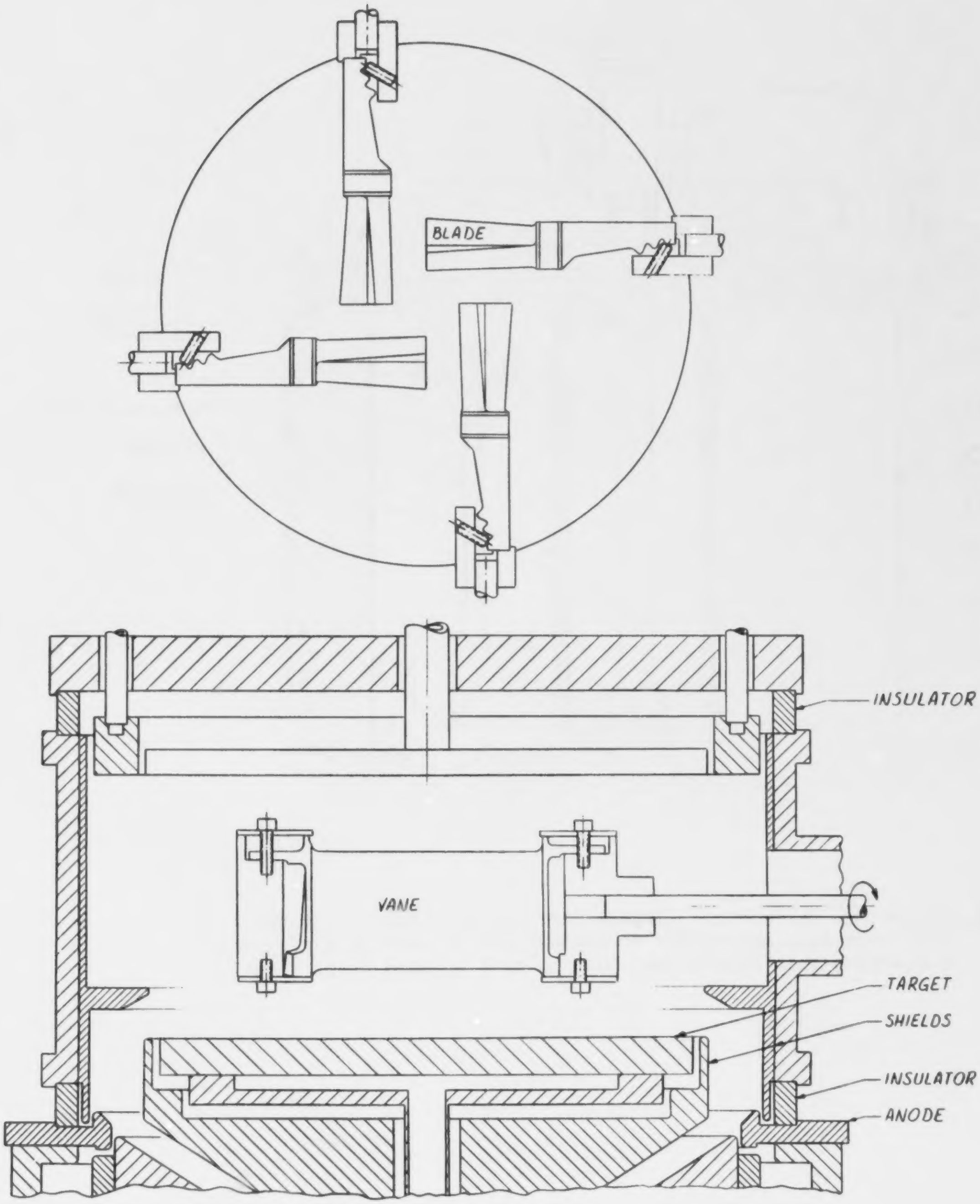


FIGURE 10. Flat-Plate Target-Complex Substrate Sputtering Geometry.

MASSIVE DEPOSIT OF Cu 0.1 Wt % Zr ALLOY

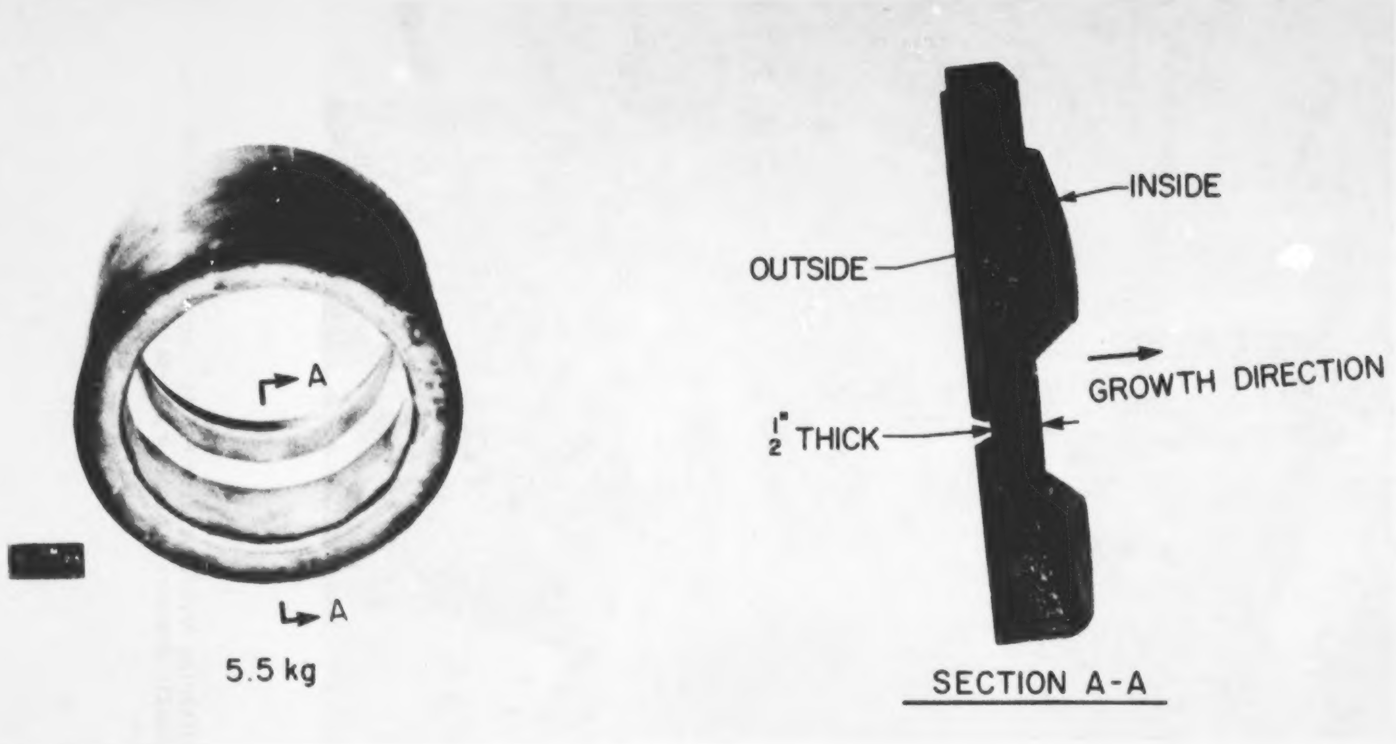


FIGURE 11. Thick Deposit for Bulk Property Testing. This material was made in four depositions, lasting 34.5, 35.5, 40 and 8 hours. The target loss was 6.3 kg and substrate gain was 5.5 kg for a net transfer efficiency of 87%. Deposition rate is about 4 mils per hour.

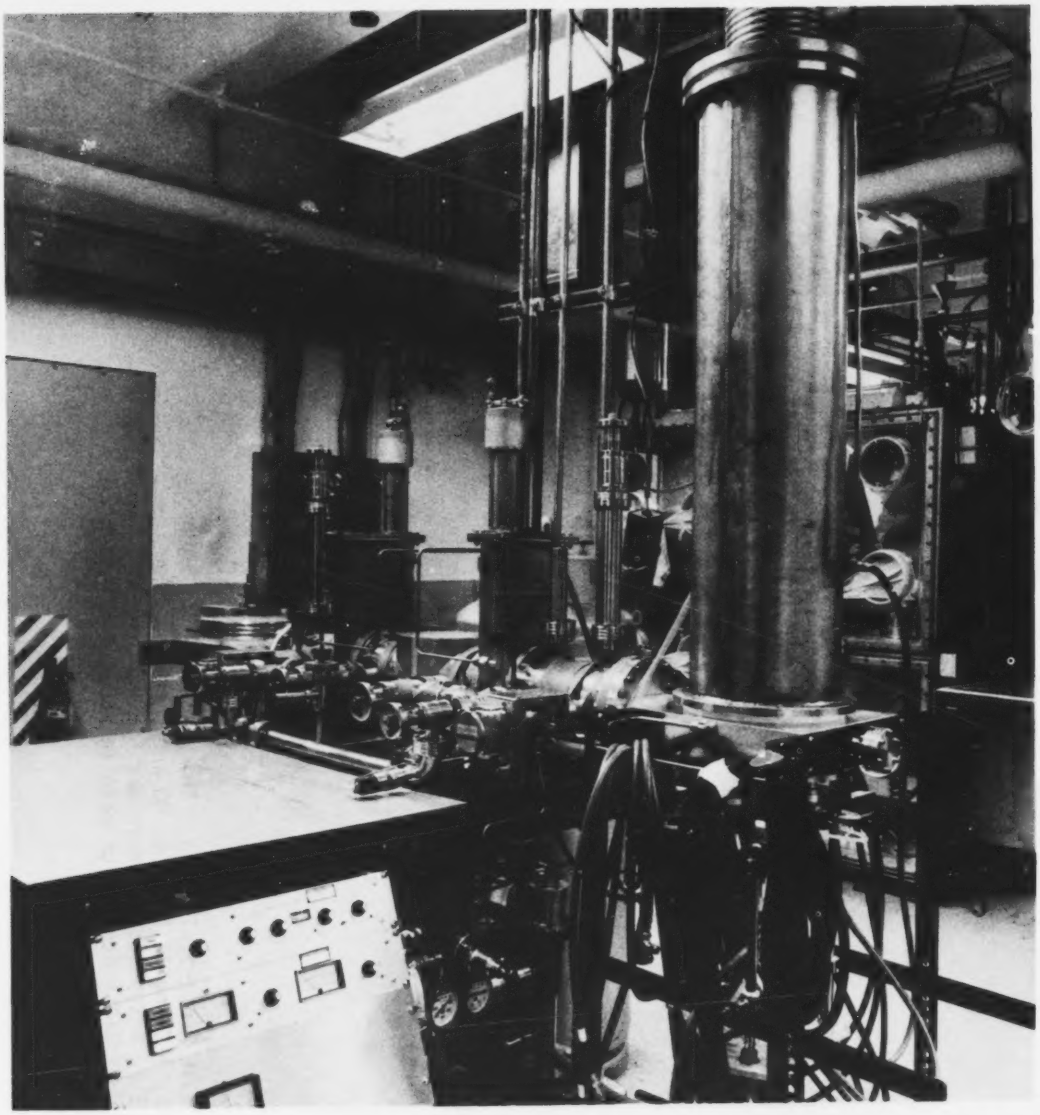


FIGURE 12. Dual-Head Sputtering Apparatus with 6.5 ft^2 Substrate Installed. Note the automatic pressure controller, by-pass valve and roughing valve.

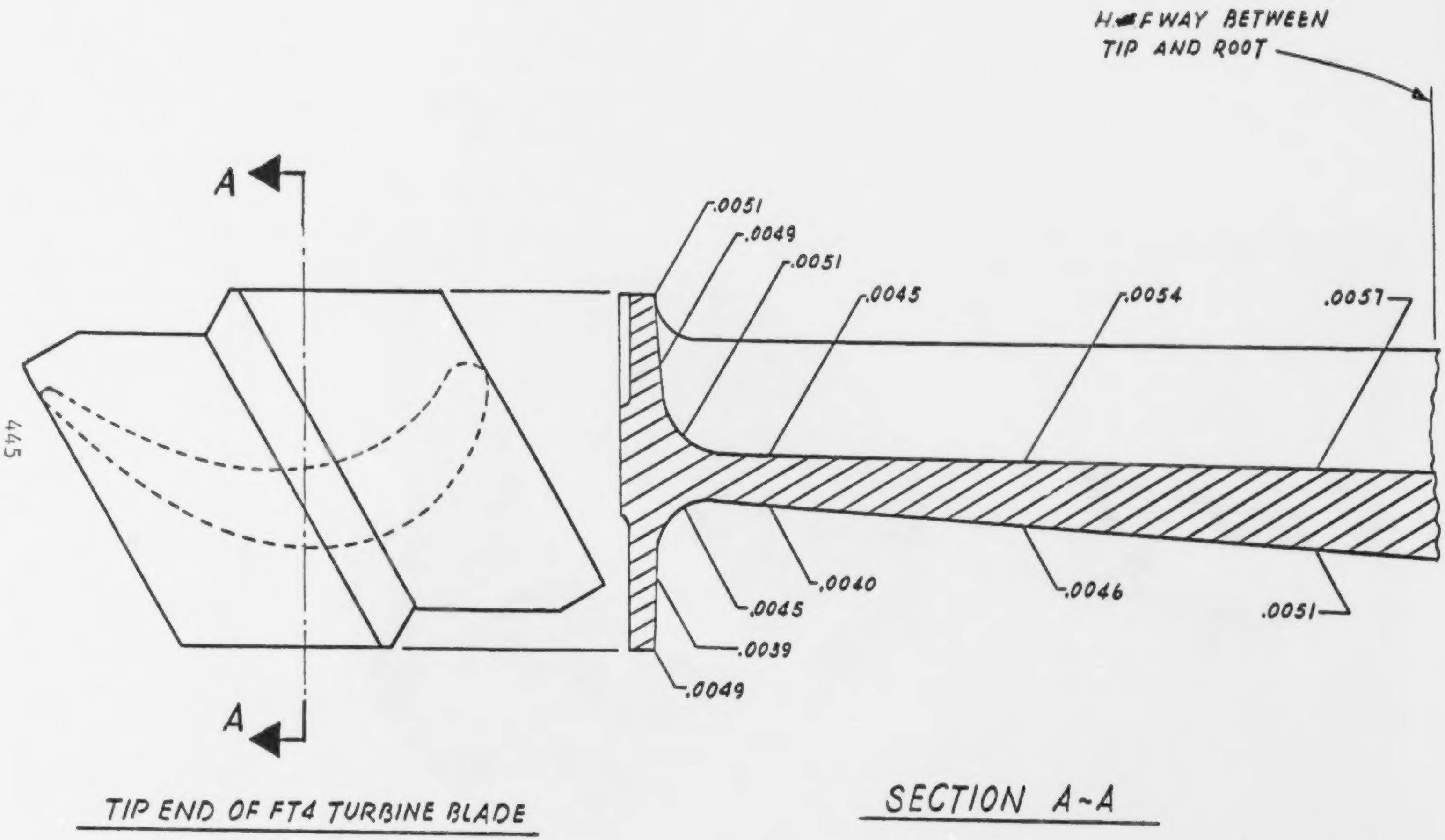


FIGURE 13. Thickness Distribution of Sputtered Coating on Turbine Blade. Coating thickness on this section varied from 0.0039 to 0.0057 inch.

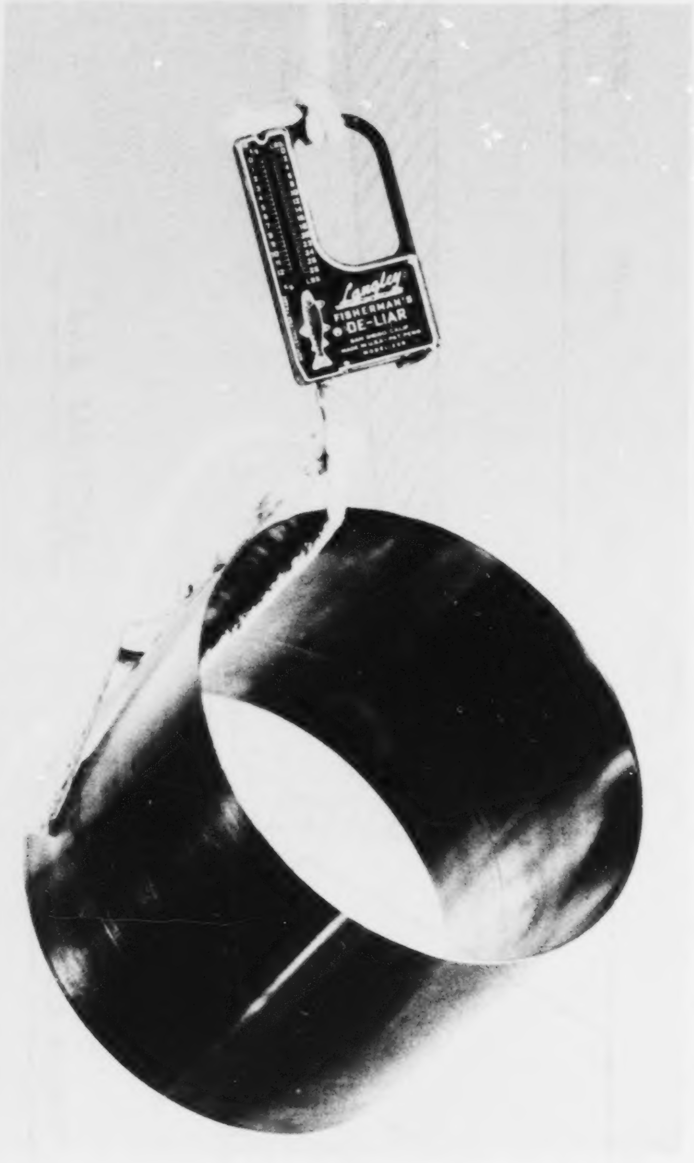


FIGURE 14. Free-Standing Sputtered Copper Cylinder. This deposit, which is over 1/8" thick was removed from its substrate by machining, producing a high-strength cylinder.

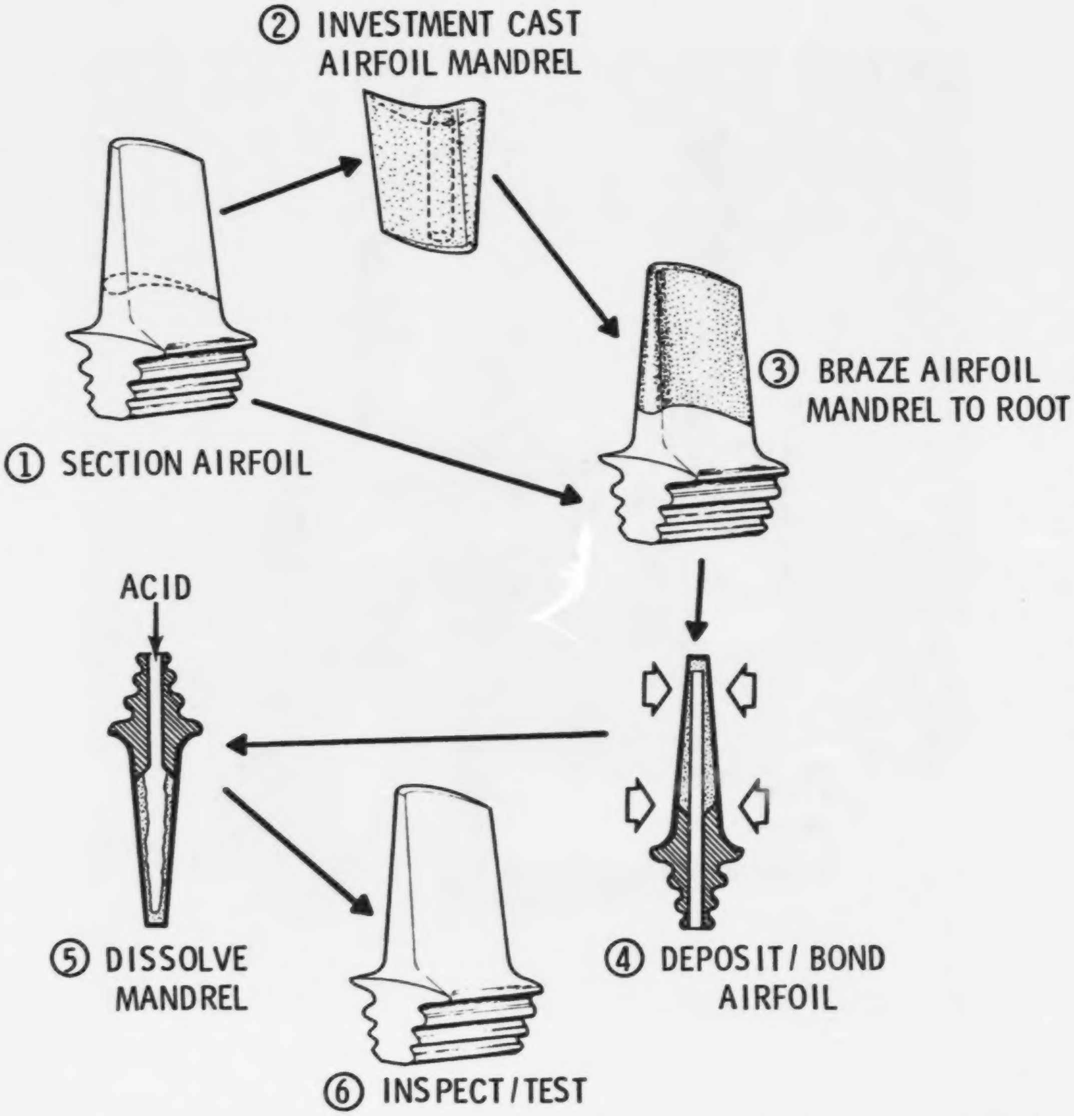


FIGURE 15. Free-Standing Turbine Blade Fabrication Sequence (soluble mandrel method). The significant improvements this process could provide are lighter mass blades with approximately the same strength.

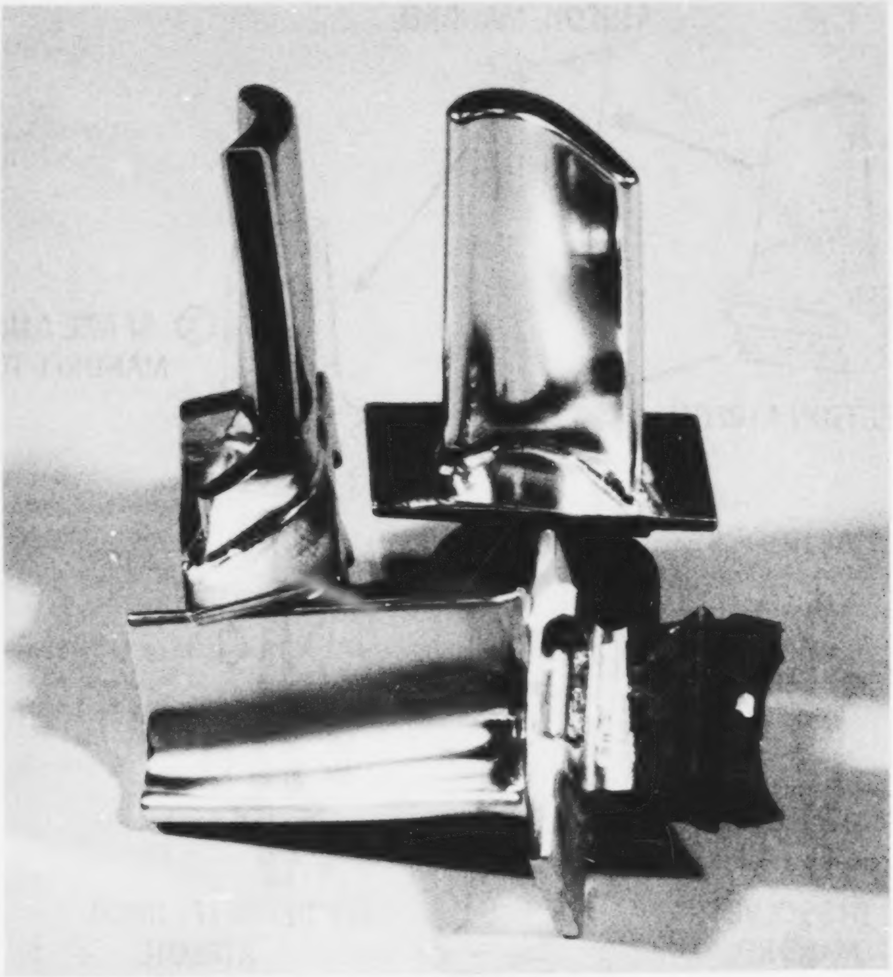


FIGURE 16. Turbine Blades Fabricated by the Soluble Mandrel Method Shown in Figure 15.

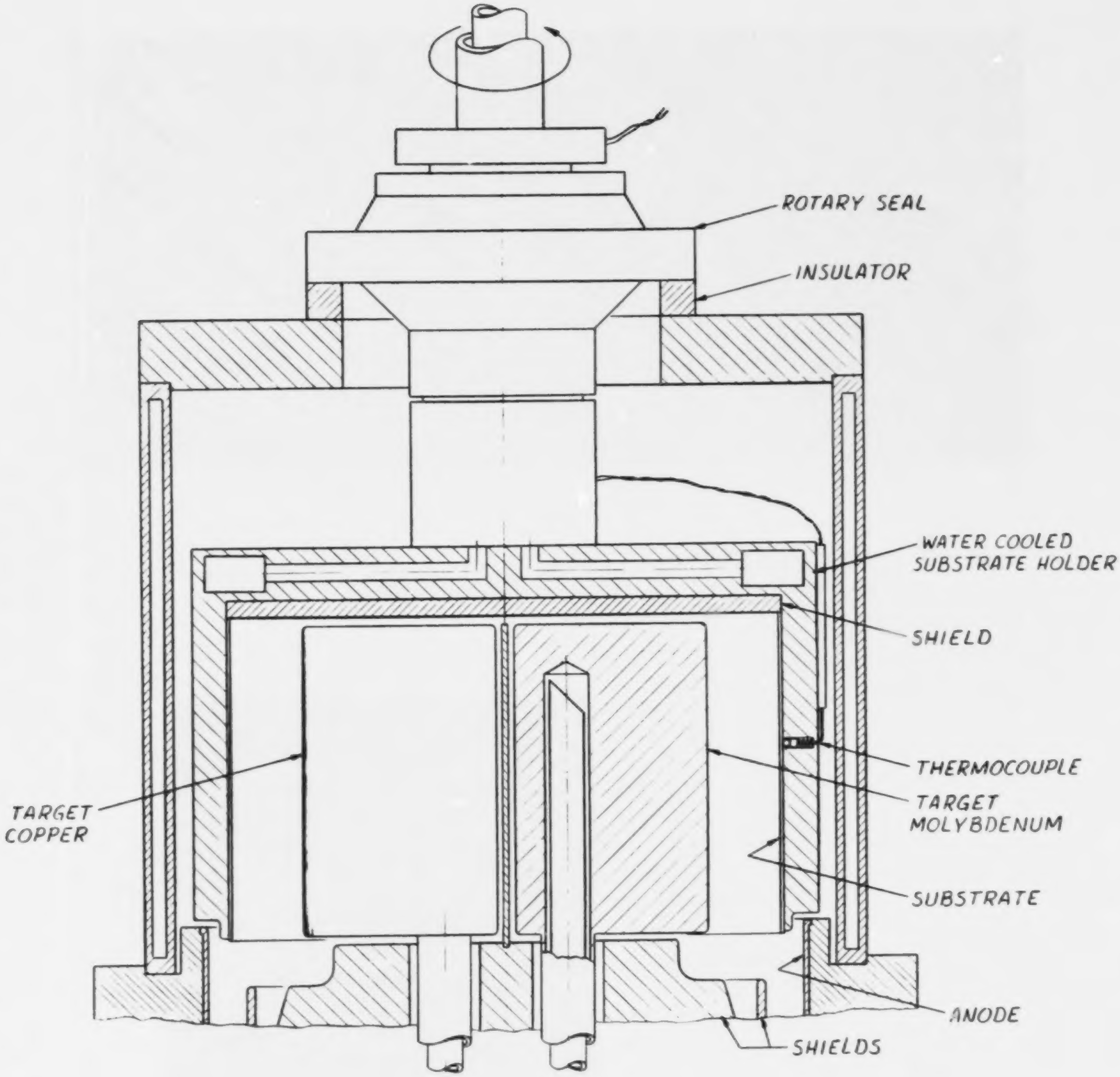


FIGURE 17. Dual Half-Cylinder Targets - Rotating Coaxial Cylindrical Substrate Sputtering Geometry for Lamellar Deposition. Layer thicknesses are controlled by the target voltages and substrate rotation speed.

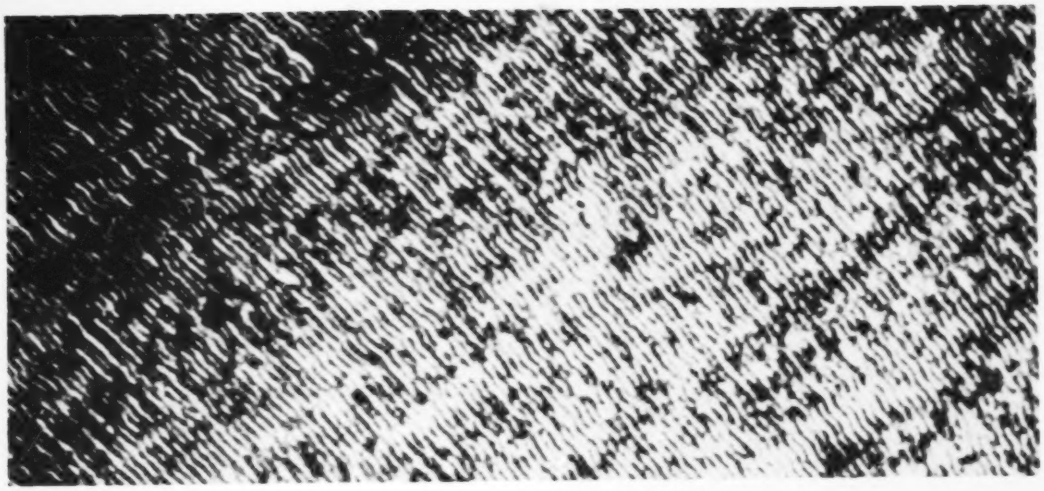


FIGURE 18. Lamellar Sputtered Deposit Micrograph. This deposit is alternate layers of Cu and Mo, approximately 80 Å in thickness. (100,000X)

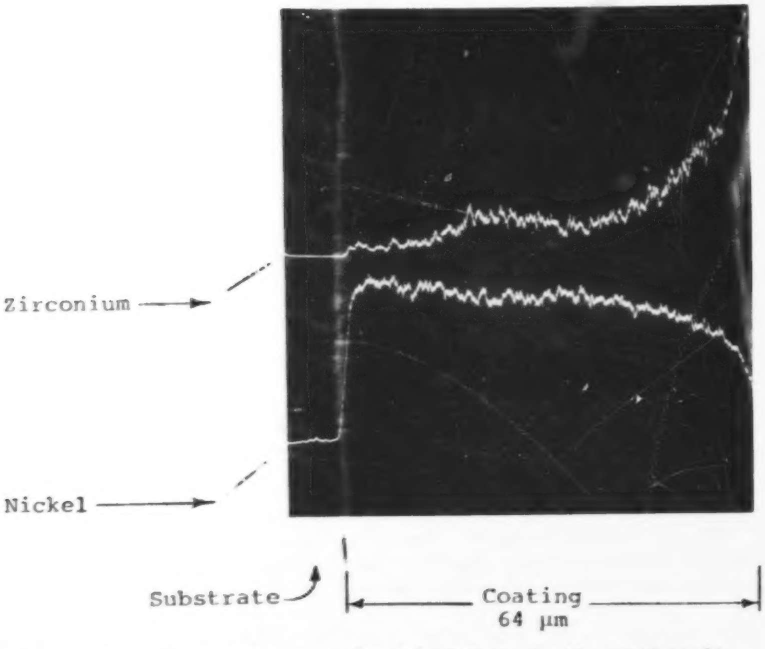


FIGURE 19. Microstructure and Composition of Graded Ni-ZrO_2 Sputtered Deposit. The deposit is graded in composition to improve adherence and to reduce the thermal expansion mismatch between the copper substrate and ceramic outer layer. Scanning Electron Micrograph (1200X)

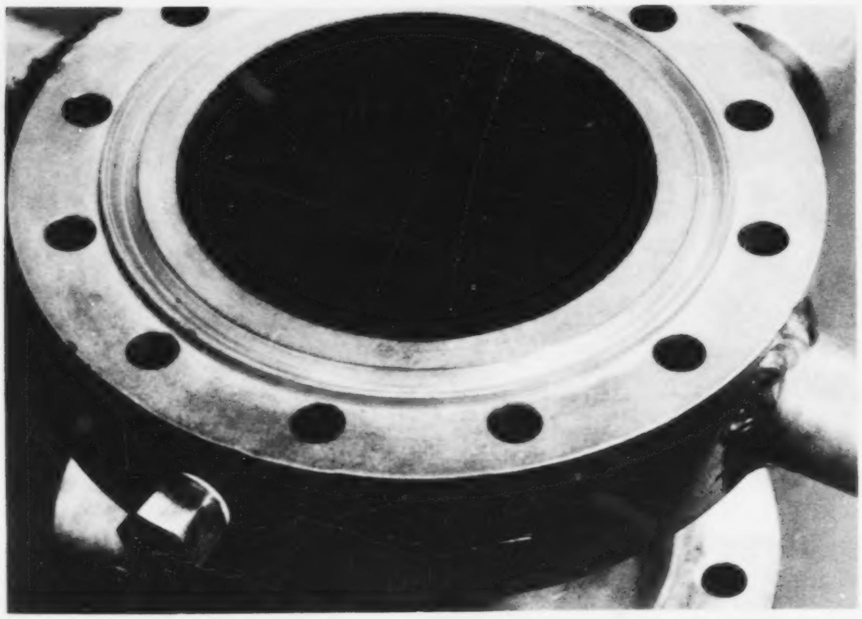
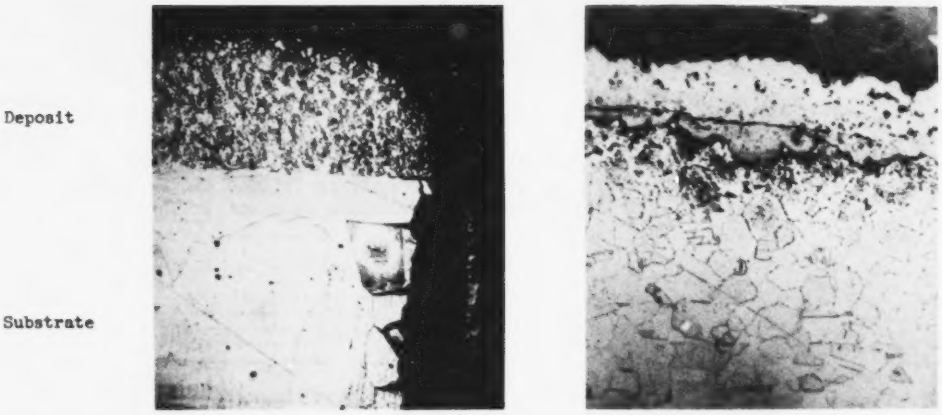


FIGURE 20. Rocket Thrust Chamber Simulator with Graded Ni-Al_2O_3 Sputtered Deposit. The deposit was adherent, smooth-surfaced and grey-black in color. This deposit just approached pure ceramic.

FIGURE 21. Demonstration of Deposit-Substrate Bond Strength. A titanium bond coat (< 0.001" thick) was sputter deposited onto a ceramic substrate, followed with about 0.015" of copper. The stress induced separation did not occur at either the copper-titanium interface or titanium-ceramic interface. Rather, the fracture occurred about ≈ 0.08" inside the ceramic substrate. Shown is the fractured ceramic substrate (right) and the back side of the deposit (left) with the layer of ceramic material attached.

Wrought 304 stainless steel oxidized in air at 2200°F for 16 hr. The normal temperature limit of resistance to progressive scaling in air for 304 stainless steel is 1700°F. Magnification 30 times.

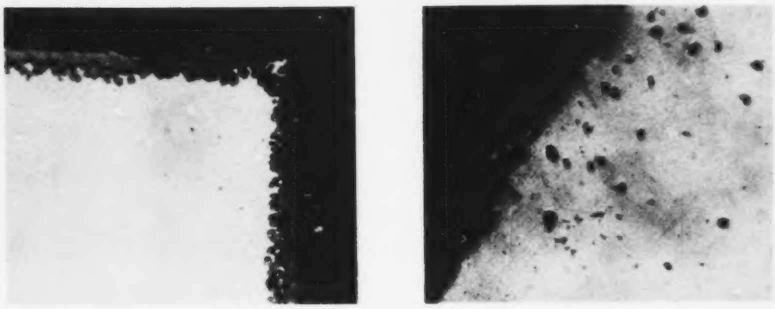
Sputtered 304 stainless steel oxidized in air at 2200°F for 16 hr. Although the composition is the same, the sputter-deposit oxidized much less than the wrought specimen (1.6 mils vs 23 mils). Magnification 30 times.



304 stainless steel sputter-deposit on a wrought 304 stainless steel substrate. Oxidized in air at 1850°F for 60 hr. The fine-grained sputter-deposit was significantly more oxidization resistant than the coarse-grained substrate. Magnification 100 times.

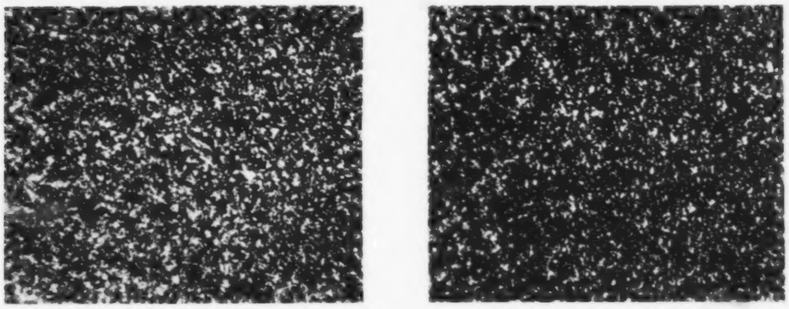
Higher magnification (500X) micrograph of the sputter-deposit oxidized at 2200°F for 16 hr. showing the oxide layer and the oxide/metal interface. The oxide on the sputter-deposit was more adherent and had a higher Cr content than the oxide on the wrought specimen. Note also that the sputter-deposit is still fine-grained.

FIGURE 22. Effect of Sputter-Deposition on the Oxidation Resistance of Theramally-Cycled 304 Stainless Steel.



SPUTTER-DEPOSITED Ni-20Cr CONTAINING 5 VOL% ALUMINA. OXIDIZED IN AIR AT 1100°C FOR 48 HR. NOTE THE ADHERENT OXIDE LAYER AND THE ABSENCE OF GROSS INTERNAL OXIDATION. 1000X

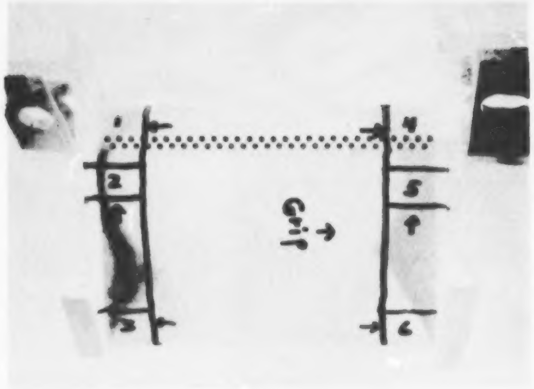
WROUGHT Ni-20Cr. OXIDIZED IN AIR AT 1100°C FOR 48 HR. NOTE THE NONADHERENT OXIDE SCALE AND THE GROSS INTERNAL OXIDATION. 1000X



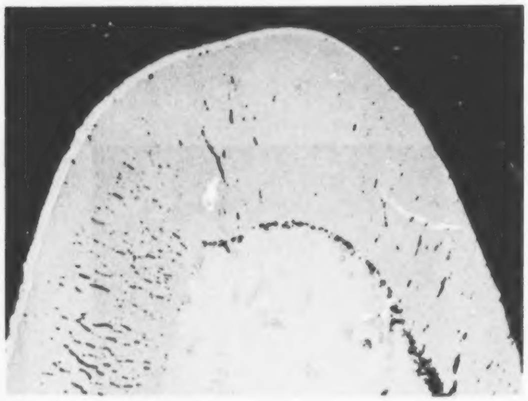
SPUTTER-DEPOSITED Ni-20Cr CONTAINING 5 VOL% ALUMINA. ANNEALED AT 1100°C FOR 15 MIN. NOTE THE FINE, EQUIAXED GRAIN STRUCTURE. 1000X

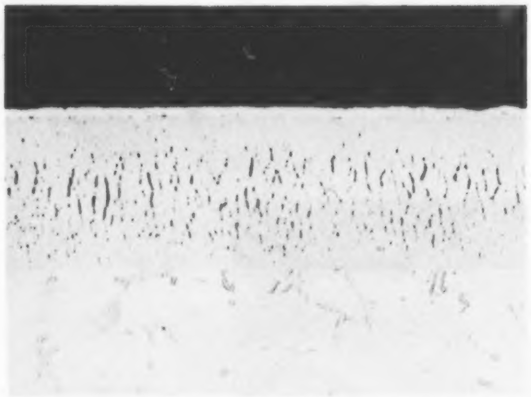
SPUTTER-DEPOSITED Ni-20Cr CONTAINING 5 VOL% ALUMINA. ANNEALED AT 1100°C FOR 48 HR. NOTE THE MICROSTRUCTURAL STABILITY OF THE SPUTTER-DEPOSITED MATERIAL. 1000X

FIGURE 23. Oxidation Resistance and Microstructure of Sputter-Deposited Ni-20Cr Containing Alumina.

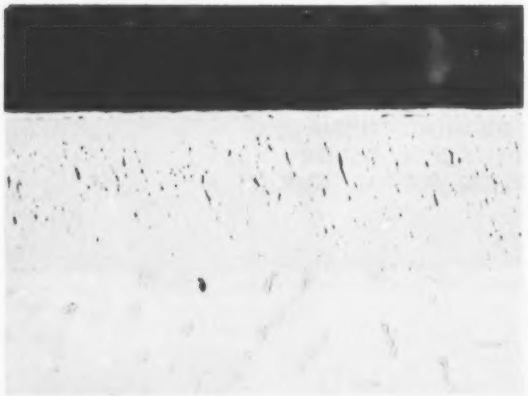


VANE # TOP VIEW

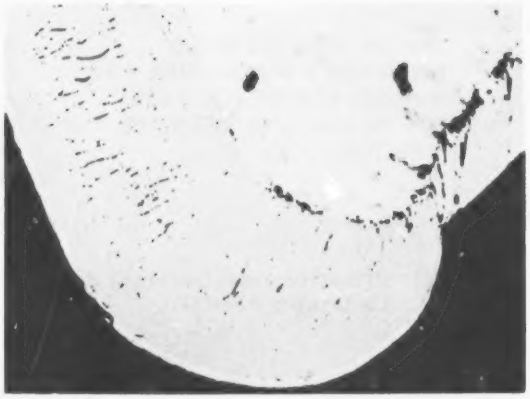




VANE # 1-6 (TOP) **250X**

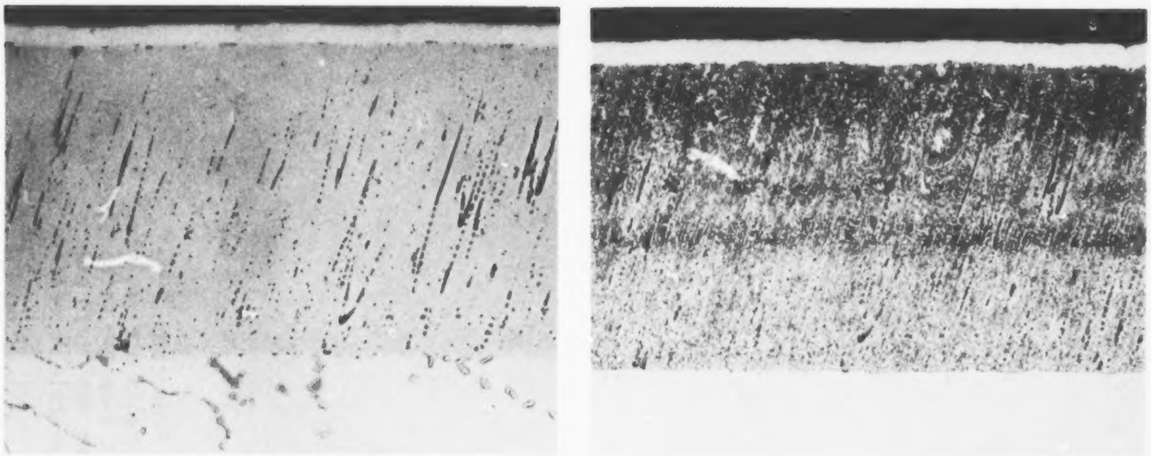


VANE # 1-6 (BOTTOM) **250X**



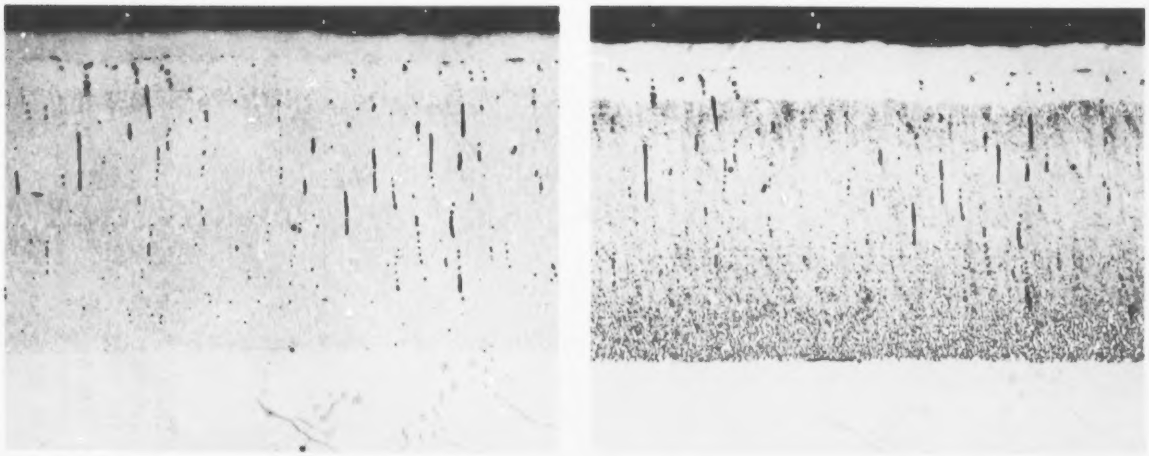
VANE # 1-6 (BOTTOM-END) **250X**

FIGURE 24. Platinum Sputtered Overlayer on Vapor-Deposited CoCrAlY. Coating is on vapor deposited CoCrAlY. Coating is on an FT-4 Turbine Vane. Micrographs are from Zone 6 (top left) and show the platinum coverage around the trailing edge.



VANE #34-2 **425X**
(TOP-AS POLISHED BEFORE H.T.)

VANE #34-2 **425X**
(TOP-ETCHED BEFORE H.T.)



VANE #34-7 **425X**
(TOP-AS POLISHED AFTER H.T.)

VANE #34-7 **425X**
(TOP-ETCHED AFTER H.T.)

FIGURE 25. Effect of Post-Deposition Heat Treatment on a Sputtered Platinum Overlayer on Vapor Deposited CoCrAlY. Coating is on an FT-4 Turbine Vane. Note the diffusion of the platinum into the CoCrAlY after 4 hours at 1080°C.

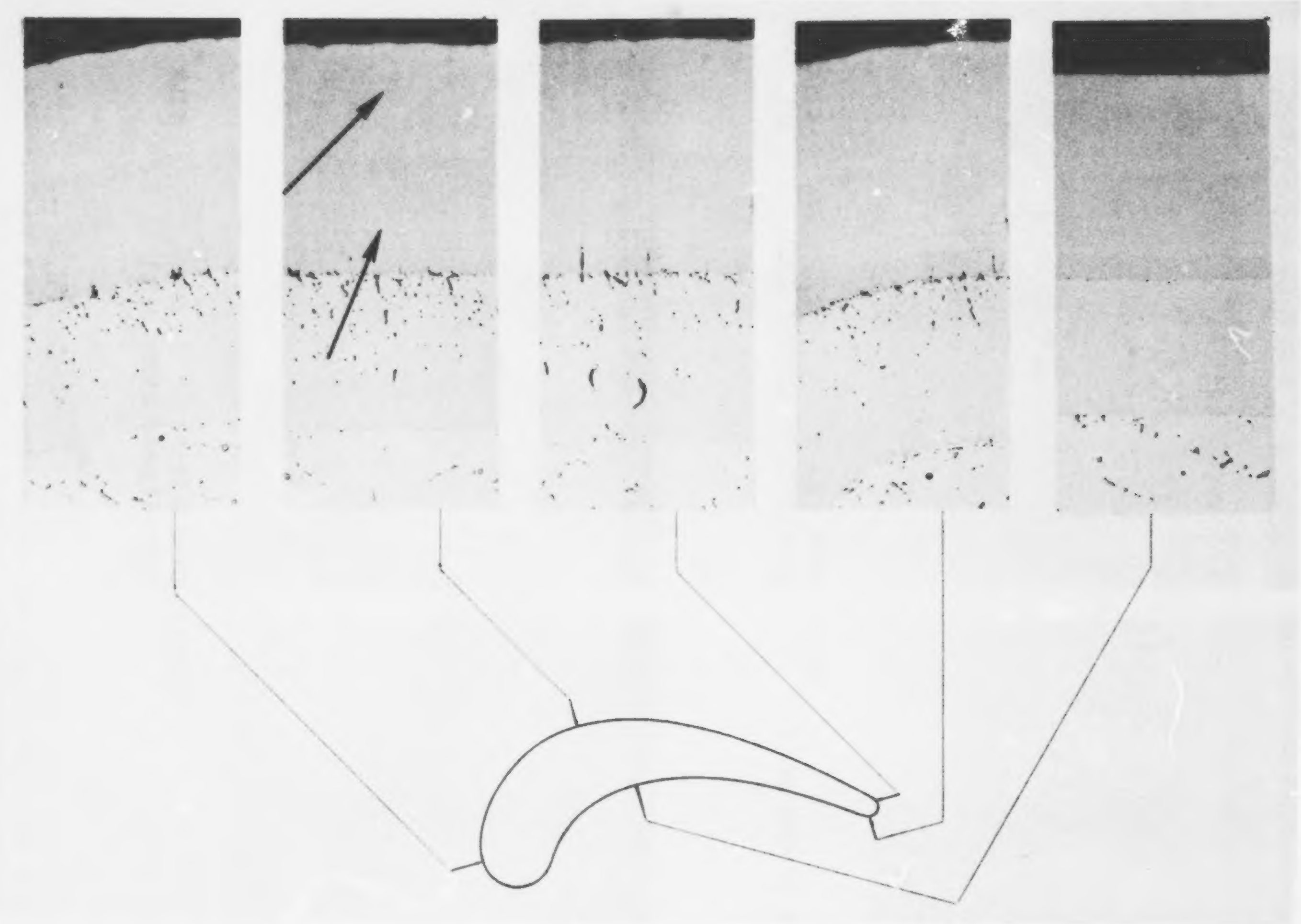


FIGURE 26. LM2500 Blade with Sputtered CoCrAlY Coatings over a Production PVD CoCrAlY Coating. Sputtered coatings from two experiments are visible. The first (bottom arrow) has a high aluminum content than the second (top arrow). Two interruptions occurred early during the first experiment (bottom arrow) and these produced the two visible interfaces in this coating.

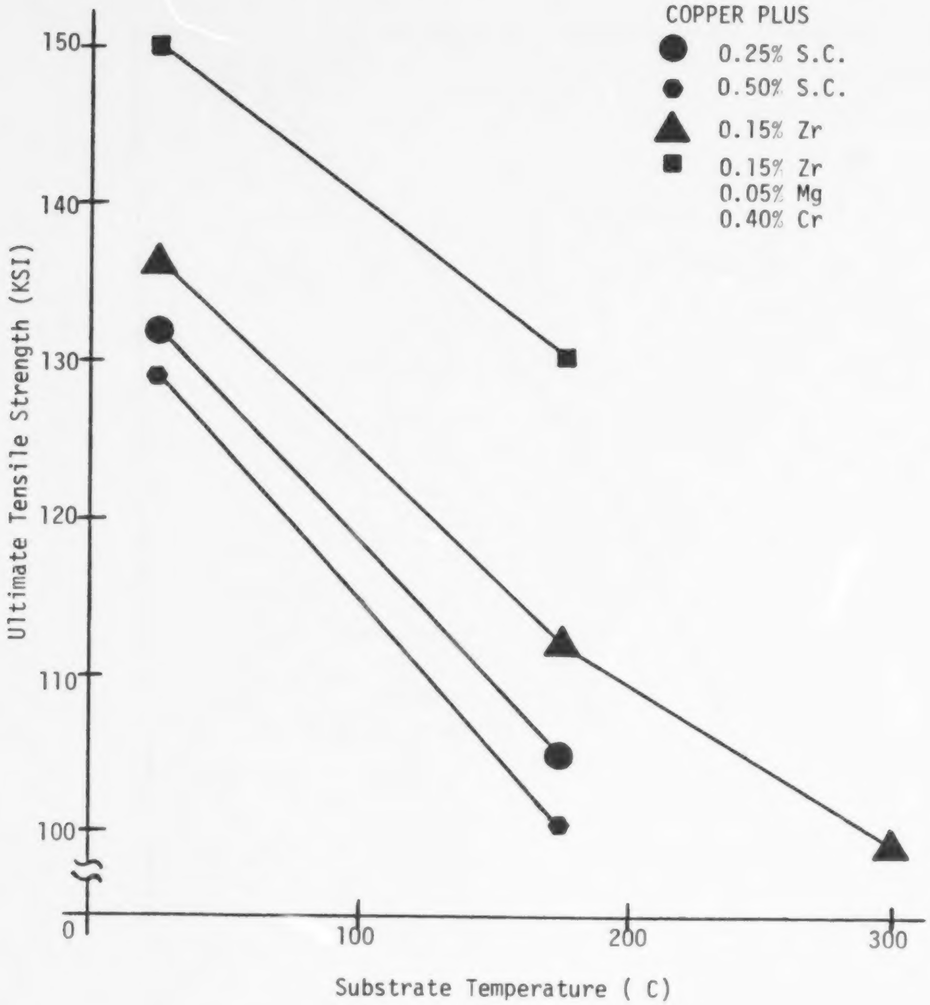


Figure 27. Tensile Strength vs. Substrate Deposition Temperature for Several Copper Alloys. The decrease in tensile strength with increasing substrate temperature is the result of two factors -- an increase in grain size and a coarser distribution of the second phase. Both factors depend upon the amount of diffusion occurring on the surface of the growing deposit before the structure is "frozen in."

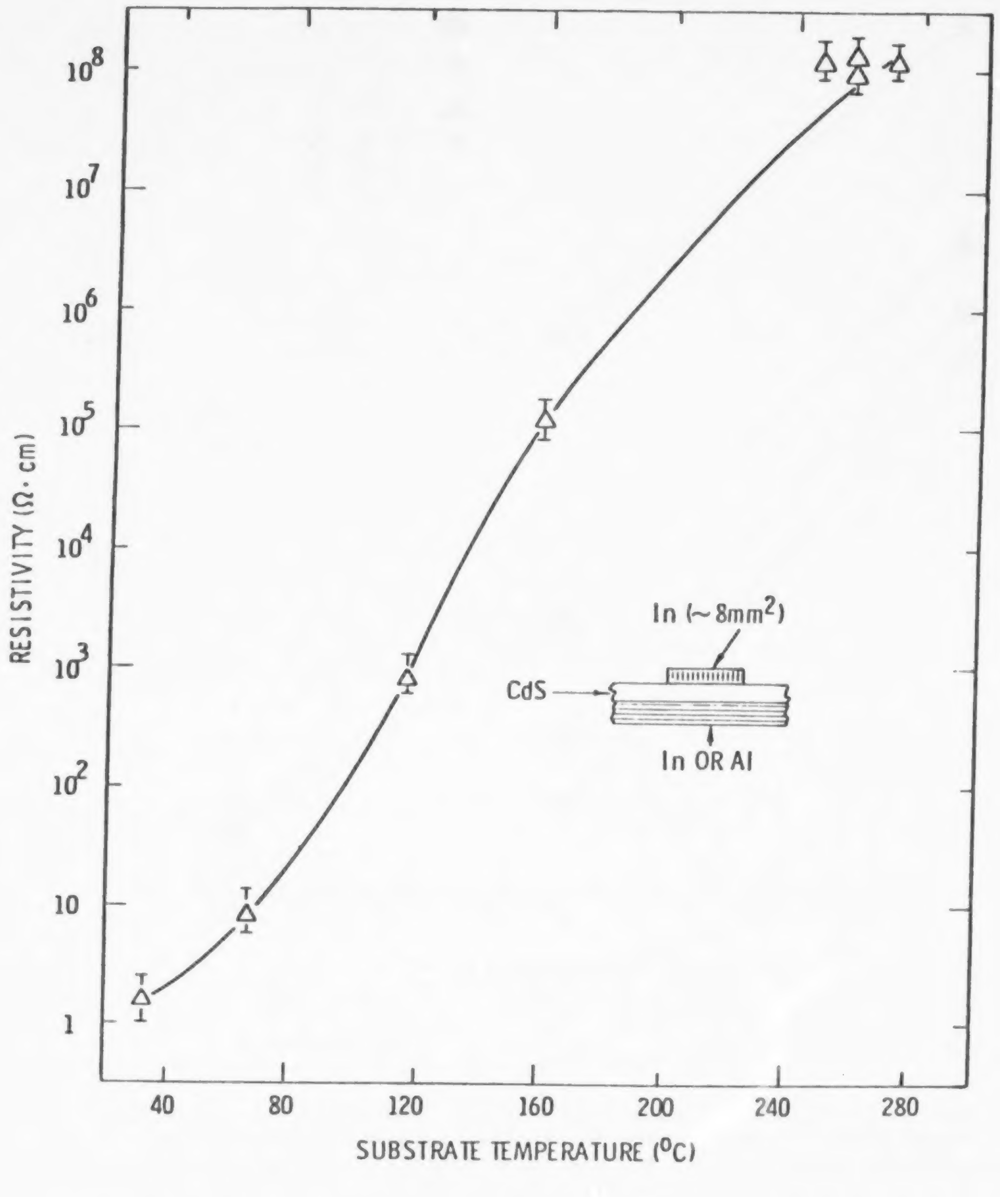


FIGURE 28. Influence of Substrate Temperature on the Electrical Resistivity of Sputtered CdS.

Appendix

SPUTTERING RELATED PUBLICATIONS AND REPORTS TO SPONSORS ON WORK PERFORMED BY BATTELLE-NORTHWEST

Sponsor: US Atomic Energy Commission

ED McClanahan, RW Moss and R Busch. Application of Sputtering to the Fabrication of Neutron Detector Anodes, BNWL-553, November 1967.

SD Dahlgren. Replica Electron Micrographs of a Sputtered Delta-Stablized Pu Alloy, J.Nucl. Mater., 333, 1968.

SD Dahlgren and ED McClanahan. High-Rate Sputtering of Stainless Steel, Proceedings of Third Symposium on the Deposition of Thin Films by Sputtering, Rochester, NY, Sept. 9-10, 1969.

SD Dahlgren, ED McClanahan, JW Johnston, and AG Graybeal. Microstructure of Sputter-Deposited 304L Stainless Steel, J.Vac Sci and Tech., vol. 7, No. 3, pp. 398-402, May/June 1970.

SD Dahlgren and AG Graybeal. Reduced Nickel Concentration in a Stainless-Steel Deposit from Bias Sputtering, J.Applied Physics, 41, No. 7, 3181, June 1970.

SD Dahlgren. Equilibrium Phases in 304L Stainless Steel Obtained by Sputter-Deposition, Metallurgical Transactions, vol. 1, pp. 3095-3099, Nov. 1970.

SD Dahlgren. Production of Smooth Deposit Thickness Profiles and Homogeneous Alloys from Parallel Strip Sources, J.Applied Physics, 41, No. 12, pp. 5004-5008, November 1970.

GL Guthrie, B Mastel, HE Kissinger and ER Bradley. Absence of Voids in Neutron Irradiated Sputtered Nickel, J.Nuc. Matls, 37, pp. 343-344, 1970.

MD Merz and SD Dahlgren. Tempering Behavior of Iron-Carbon Sputter Deposits with 0 to 5 wt% C, Met. Trans. 2, p. 3123, 1971.

N. Laegreid and SD Dahlgren. Wall Sputtering and Wall Life Criteria, Summary of Meeting, Fusion Reactor First Wall Materials, USAEC Report WASH-1206, Germantown, MD, p. 69, Jan. 1972.

N. Laegreid and SD Dahlgren. Controlled Thermonuclear Reactor First Wall Sputtering and Wall Life Estimates, J.Appl. Phys., 44, 2093, 1973.

SD Dahlgren and DM Kroeger. High Critical Current Densities Found for Thick $Nb_{12}Al_3Ge$ Superconducting Deposits Made by High-Rate Sputtering, J.Appl. Phys., vol. 44, No. 12, pp. 5595-5598, December 1973.

SD Dahlgren. High-Rate Sputtering of Nb-Al-Ge and Nb-Al Superconductors, September 30, 1974.

Sponsor: US Energy Research and Development Administration

SD Dahlgren, M. Suenaga, and TS Luhman. High Field Critical Current Densities for a Thick $Nb_{12}Al_3Ge$ Superconductor Made by High-Rate Sputtering, J.Appl. Phys., 45, 5462, 1974.

Sponsor: US Energy Research and Development Administration -- continued

R. Wang and RP Allen. Structure Transformation in Sputter-Deposited Sm_2Co_{17}, Proceedings of 20th Annual Conference on Magnetism and Magnetic Materials, pp. 683, 1974.

SD Dahlgren. High-Rate Sputtering of Nb-Al-Ge and Nb-Al Superconductors, Proceedings of the 1974 Applied Superconductivity Conference, Sept. 30 - Oct. 1-2, 1974, Chicago, Illinois, IEEE Trans on Magnetics, Vol. Mag 11, p. 217, 1975.

RP Allen, SD Dahlgren, and MD Merz. Preparation and Characterization of Thick Metastable Sputter Deposits, Proceedings of the 2nd International Conference on Rapidly Quenched Metals (Section I): MIT, Cambridge, Massachusetts, 1975.

R. Wang and MD Merz. Noncrystallinity and Polymorphism in Elemental Solids, Nature, March 1976.

R Wang and MA Bayne. Sputter-Deposited Electrical Insulators for CTR Applications, Proceedings of the 2nd Topical Meeting on the Technology of Controlled Nuclear Fusion, September 21-23, 1976, Richland, Washington, vol. II, p. 477.

RP Allen, SD Dahlgren, and R. Wang. Sputter-Deposition of Metastable Ta-Pu, Ag-Pu, and Co-Pu Alloys, Plutonium 1975 and Other Actinides, Ed. H. Blank and R. Lindner, (North-Holland Pub. Co. - Amsterdam, Oxford, American Elsevier Publishing Co., Inc., - New York), p. 61, 1976.

SD Dahlgren. High-Rate Sputter Deposition and Heat Treatment of Nb-Al-Ge and Nb-Al Superconductors, Met. Trans. A, 7A, 1375, 1976.

R. Wang and SD Dahlgren. Metastable A-15 Phase Superconductors Transformed from Metastable bcc Nb_3X Solid Solutions Made by High-Rate Sputter Deposition, Proceedings of 2nd International Conference on Rapidly Quenched Metals (Section II), MIT, Cambridge, Massacuhetts, 1975 -- MIT Press, Cambridge, Massachusetts, 1976.

WT Pawlewicz and N Laegreid. Sputter-Deposited Materials for Photovoltaic Devices, in Proceedings of the ERDA Photovoltaic Advanced Materials R&D Program Review Meeting, Washington, DC, March 1977.

R Wang and MD Merz. Polymorphic Bonding and Thermal Stability of Elemental Noncrystalline Solids, Physica Status Solidi, 39, p 697, 1977.

Sponsor: Advanced Research Projects Agency

SD Dahlgren and MD Merz. Solid Solutions in Sputter-Deposits of Iron with 0 to 5 wt% C, Metallurgical Trans., vol. 2, pp. 1753-1760, July 1971.

JW Patten, ED McClanahan, and JW Johnston. Room-Temperature Recrystallization in Thick Bias-Sputtered Copper Deposits, J.Appl. Phys., vol. 42, No. 11, pp. 4371-4377, October 1971.

SD Dahlgren and ED McClanahan. Reduced Sputtering Yields for Two-Phase Ag-Ni and Ag-Co Targets, J.Appl. Phys., vol. 43, No. 4, April 1972.

JW Patten and ED McClanahan. Effect of Substrate Bias and Deposition Temperature on the Properties of Thick Sputtered Chromium Deposit J.Appl. Phys., vol. 43, No. 11, November 1972.

JW Patten and ED McClanahan. Effects of Deposition Temperature and Substrate Bias on Orientation and Hardness of Thick Sputter Deposited Beryllium Foils J. of the Less-Common Metals, 30, pp. 351-359, 1973.

Sponsor: Advanced Research Projects Agency -- (continued)

RW Stewart. Materials Synthesis by Sputter Deposition -- December 1, 1970 to June 1, 1971

RW Stewart. Materials Synthesis by Sputter Deposition -- June 1, 1971 to June 1, 1972

RW Stewart. Materials Synthesis by Sputter Deposition -- June 1, 1972 to June 1, 1973

RW Stewart. Investigate Material Systems for Mirrors Used in High Power CO and CO_2 Lasers, Semiannual Technical Report - December 1972.

RW Stewart. Investigate Material Systems for Mirrors Used in High Power CO and CO_2 Lasers, Semiannual Technical Report - August 1973.

RW Stewart. Investigate Material Systems for Mirrors Used in High Power CO and CO_2 Lasers, Final Technical Report - November 1974.

R. Busch and JW Patten. Lamellar Composites Formed by Sputter Deposition, Annual Technical Report - June 1974.

R. Busch and JW Patten. Lamellar Composites Formed by Sputter Deposition; Properties and Potential Application to Turbine Blades, Annual Technical Report - July 1975.

R. Busch and JW. Patten. Application of Sputter-Deposited Lamellar Composite Technology to the Development of High Temperature Turbine Blade Materials and Airfoil Fabrication, Annual Technical Report - October 1976.

Sponsor: Battelle Memorial Institute

R. Wang and SD Dahlgren. Observation of Twin Faults in Sputter-Deposited High-Purity Nickel, J.of Mat. Sci., 10, 1456, 1975.

MD Merz and SD Dahlgren. Tensile Strength and Work Hardening of Ultrafine Grain Copper. J.Appl. Phys., 46, p. 3235, 1975.

MD Merz, SD Dahlgren, R. Busch and R. Wang. Mechanical Properties of Ultrafine-Grained Copper and Copper-Zirconium Sputter Deposits, Proc. 2nd intern. Conf. on Mechanical Behavior of Materials, Fed. of Mat'ls. Soc., p. 58, 1976.

SD Dahlgren, WL Nicholson, MD Merz, W. Bollmann, JF Devlin and R. Wang. Microstructural Analysis and Tensile Properties of Thick Copper and Nickel Sputter Deposits, Thin Films, 40, p. 345, 1977.

N Laegreid, R Wang and WT Pawlewicz. Fabrication of Low Cost Thin-Film Solar Cells, in Proceedings of DARPA Materials Research Council Summer Meeting, LaJolla, CA, 1974.

JW Patten. Implications of Metal Foam Experiments for Fluid Flow Effects on Materials System Processed in Zero Gravity, invited paper presented at the conference "Applications of Space Flight in Materials Science and Technology," NASA and NBS, National Bureau of Standards, Gaithersburg, MD, April 1977, extended abstract published in Proceedings.

JW Patten. Materials Processing in Space, invited paper presented at the "Symposium on Use of Space Shuttle for Science and Engineering," NASA and AVS, Ames Research Center, Mountain View, CA, May 1977, extended abstract published in Proceedings.

Sponsor: Naval Ship Engineering Center (Naval Sea Systems Command)

ED McClanahan, RW Moss, R Busch, JW Patten, JW Johnston, IB Mann and HR Gardner. Investigate Feasibility of Using Sputter Deposition to Produce an Adherent Sulfidation Resistant Coating of CoCrAlY on Superalloy Turbine Components to be Service Tested by NAVSEC. Two-Qtr Report - February 2, 1973 to August 6, 1973.

JW Patten, ED McClanahan, RW Moss, DD Hays, JW Johnston, LK Fetrow, and HR Gardner. Investigate Feasibility of Using Sputter Deposition to Produce an Adherent Sulfidation Resistant Coating of CoCrAlY on Superalloy Turbine Components to be Service Tested by NAVSEC. Report Period - August 7, 1973 to March 28, 1974.

ED McClanahan, R. Busch, JW Patten (BNW), and J Fairbanks (NAVSEC). Initial Work on the Application of Protective Coatings to Marine Gas Turbine Components by High-Rate Sputtering, ASME publication #74-GT-100. Presented at the Gas Turbine Conference and Products Show, Zurich, Switzerland, March 30 - April 4, 1974.

JW Patten, ED McClanahan, RW Moss, JW Johnston, and RA Lundgren. Preliminary Report on the Sputter Deposition of Platinum Coatings on Superalloy Pins. Report Period - July 1, 1973 to September 15, 1973.

DD Hays and JW Patten. Burner Rig Testing of Sputter-Deposited and Physical Vapor Deposited CoCrAlY Coatings. Report Period - February 27, 1975 to January 15, 1976.

JW Patten, RW Moss, DD Hays, ED McClanahan, RA Lundgren and HR Gardner. Extend CoCrAlY and Pt Sputter-Deposition Technology to Provide Coatings on FT4 Turbine Vanes for At-Sea Evaluation. Report Period - February 27, 1975 to January 15, 1976.

JW Patten, RW Moss, DD Hays, ED McClanahan and RA Lundgren. Extend CoCrAlY and Pt Sputter-Deposition Technology to Provide Coatings on FT4 Turbine Vanes for At-Sea Evaluation. Report Period January 16, 1976 to December 31, 1976.

JW Patten, DD Hays, RW Moss (Battelle-Northwest), JW Fairbanks (NAVSEC). Recent Development in the Application of High-Rate Sputtering Technology to the Formation of Hot Corrosion-Resistant Metallic Coatings on Marine Gas Turbine First-Stage Vanes and Blades, contributed by the American Society of Mechanical Engineers for presentation at 1977 Tokyo Joint Gas Turbine Congress held in Tokyo, on May 22 to 27, 1977 under the co-sponsorship of Gas Turbine Society of Japan, the Japan Society of Mechanical Engineers and the American Society of Mechanical Engineers.

R Busch, RW Moss and HG Barrus. Investigate Feasibility of Using Sputter Deposition to Produce an Adherent Zirconia (ZrO_2) Coating on Superalloy Test Pins for Evaluation by NAVSEC in a Burner Rig. Two-Qtr Report - May 5, 1973 to November 4, 1973.

R Busch, RW Moss, and HG Barrus. Investigate Feasibility of Using Sputter Deposition to Produce an Adherent Zirconia (ZrO_2) Coating on Superalloy Test Pins for Evaluation by NAVSEC in a Burner Rig. Report Period - November 5, 1973 to March 28, 1974.

R Busch. Develop Sputter Deposited, Graded Metal-ZrO_2 Coating Technology for Application to Turbine Hot Section Components. Report Period - February 27, 1975 to November 20, 1975.

R Busch. Develop Sputter Deposited, Graded Metal-ZrO_2 Coating Technology for Application to Turbine Hot Section Components. Report Period - November 21, 1975 to September 30, 1976.

Sponsor: Northwest Mutual Life Insurance Company/Battelle Memorial Institute

WT Pawlewicz, RP Allen, HG Barrus and N Laegried. Structure and Properties of Sputter-Deposited CdTe, Proceedings 2nd International Conference Cadmium Telluride, Strasbourg, France, in Revue de Physique Appliquee, vol. 12, No. 2, 417-422, February 1977.

Sponsor: Air Force Materials Laboratory (AFML) - Wright Patteron Air Force Base

MD Merz, RP Allen and SD Dahlgren. Elastic Constant Increases Upon Crystallization of a Sputter Deposited Amorphous Alloy, J. Applied Physics, Sept. 1974.

RD Nelson. Research in the Production of Rare-Earth-Cobalt Permanent Magnet Material by Sputter Deposition, May 1974.

Sponsor: Rock Island Arsenal

RH Jones, RW Moss, ED McClanahan and HL Butts. The Sputter Deposition and Evaluation of Tungsten and Chromium Coatings for Use in Small Arms Components, December 18, 1974.

RH Jones. An Evaluation of Chromium Deposited by High-Rate Sputtering, Metallurgical Transactions, vol. 7A, pp. 1333-1339, September 1976.

Sponsor: NASA-Lewis Research Center

ED McClanahan, R. Busch and RW Moss. Property Investigation and Sputter Deposition of Dispersion-Hardened Copper for Fatigue Specimen Fabrication, November 12, 1973.

R. Busch and MA Bayne. Development of Sputtered High Temperature Coatings for Thrust Chambers, August 9, 1976.

Sponsor: NASA-Space Processing Program

JW Patten and EN Greenwell. Feasibility of Producing Closed-Cell Metal Foams in a Zero-Gravity Environment from Sputter-Deposited Inert Gas-Bearing Metals and Alloys (74-10), Post-Flight Technical Report, SPAR Flight #1, April 8, 1976.

JW Patten and EN Greenwell. Feasibility of Producing Closed-Cell Metal Foams in a Zero-Gravity Environment from Sputter-Deposited Inert Gas-Bearing Metals and Alloys. (74-10), Post-Flight Technical Report, SPAR Flight #2 and Final Report, December 20, 1976.

JW Patten and EN Greenwell. Closed-Cell Foams Produced from Sputter-Deposited Aluminum, Proceedings AIAA 15th Aerospace Sciences Meeting, Los Angeles, California, January 24-26, 1977.

Sponsors: Advanced Research Projects Agency, US Atomic Energy Commission (Div. of Physical Research), and Battelle Memorial Institute

R. Busch and ED McClanahan. Copper-Base Materials Formed by High-Rate Sputtering, Technical Report - March 1977.

Evaluation of Alternatives

Session V

Thursday Morning 9:30

CADMIUM AS A COMMODITY

John M. Lucas
John M. Hague
U. S. Bureau of Mines
Washington, D.C. 20241

Cadmium is associated geochemically with zinc ores and is separated by necessity as a byproduct of zinc mining and processing. Until 1975 when Japan became the world's major producer of cadmium, the United States was the largest producer. The United States continues to consume more than any other nation, about 30 percent of world supply. In the United States six companies are primary producers of cadmium metal, and two of these also produce cadmium oxide and other compounds. Other nations with major cadmium metal production are the U.S.S.R., Canada, Federal Republic of Germany, and Belgium. Ore reserves available to domestic producers are a function of zinc ore reserves, and future resources will probably continue to be closely related to zinc development projects. Cadmium-zinc resources exist on all continents. Countries with major resources are the United States, Canada, Australia, and the U.S.S.R.

Cadmium is used for plating or coating small steel parts to impart corrosion resistance. It is a component of nickel-cadmium and silver-cadmium batteries. Cadmium compounds form yellow and red pigments and serve as heat stabilizers in plastics. Cadmium is used in fluorescent phosphors, low-melting alloys, as a hardener for copper wire, and in nuclear reactor control rods. In some electroplating applications, zinc can be substituted for cadmium, and in some pigments iron or zinc compounds can be used for red or yellow, but they are not as brilliant nor as stable as cadmium compounds.

Much of the research on cadmium has dealt with its toxic effects on human health and the environment. Cadmium has been identified by the Environmental Protection Agency (EPA) as a dangerous toxic pollutant.

Looking forward to 2000, U.S. cadmium production, which is related to zinc production, may reach 5,000 tons per year. Demand is expected to grow at about 3 percent per year and remain at least twice the domestic production.

Preceding page blank

CADMIUM AS A COMMODITY

By John M. Lucas and
John M. Hague
U.S. Bureau of Mines
2401 E St., NW.
Washington, D.C. 20241

Cadmium, like many widely used and accepted metals, is used in a multitude of necessary though obscure applications. Daily, we unconsciously rely upon cadmium and its numerous compounds to protect our metal goods from damaging corrosion, to power our portable radios and calculators, and to protect our living, working, and storage spaces from the ravages of fire.

Historical Review

This useful metal was discovered in 1817 by F. Strohmeyer, a professor of metallurgy at Germany's Goettingen University. During a routine examination the professor noticed an unusual slightly yellow coloration in a sample of calamine or zinc carbonate, obtained for testing from the zinc works at Salzgitter, Germany. After thoroughly testing the sample for the presence of iron or other known elements which may also produce a yellow stain the professor rightly concluded that the negative results of his tests indicated the presence of a new element. Further testing confirmed his suspicion and cadmium was thus added to the rapidly expanding list of newly discovered elements. Strohmeyer's serendipitous discovery only slightly preceeded the nearly simultaneous detection of cadmium by other independent analysts. Therefore, the name "cadmium" proposed by the professor fortunately took precedence over other names such as jumonium, melinum, or klaprothium suggested by the other, later discoverers.

Few practical applications were immediately found for the new metal and for a period of over 60 years following its discovery Germany was the only country producing significant quantities of cadmium on a commercial basis. Commercial production of the metal commenced in the United States in 1907 and by the beginning of the First World War a number of domestic smelters were recovering cadmium as a byproduct of their zinc smelting operations. Following the wartime termination of trade with Germany, production of cadmium in the United States expanded rapidly and by 1917 this country was the world's leading producer of the refined metal, a position that was retained until 1975.

During the First World War cadmium was employed as a substitute for scarce tin in the production of solders and other alloys. This usage, together with the development of a practical commercial cadmium electroplating process by the Udylite Company in 1919, greatly stimulated the uses of cadmium throughout the industrialized world. Today, due to the importance of minimizing corrosion, cadmium electroplating plays an important role in both the developed and developing nations of the world.

Physical Properties and Occurrence

Cadmium is a soft, malleable metal slightly heavier than iron. A freshly cut surface exhibits a silvery-white color tinged with blue. This bright surface when exposed to a humid or corrosive atmosphere will quickly develop a thin dull protective coating of cadmium oxide. The metal, in the vapor or compound form, is toxic and must be handled with care to avoid acute exposure and accidental release to the environment.

When compared with many of the metals commonly used in modern industry cadmium is a relatively rare element. Of the nearly 100 naturally occurring elements, cadmium ranks 66th in order of abundance and on the average the earth's crust contains less than two parts of cadmium in 10 million. For the most part, cadmium occurs combined with various types of zinc ores. The most common cadmium mineral, greenockite, a cadmium sulfide, occurs as a yellow coating or stain on the principal zinc mineral sphalerite, or zinc sulfide. Greenockite may have been the yellow mineral which earlier had captured the attention of Professor Strohmeyer. Cadmium minerals may occur to a lesser extent with lead and copper ores containing zinc, however, most of the metal recovered today for commercial usage comes from smelters which deal principally with zinc sulfide ores. At these zinc smelters cadmium is usually recovered as the major byproduct metal.

The minerals of cadmium occur in nature in such small quantities that they are neither sufficiently abundant nor in quantities great enough to constitute a minable ore body.

As a byproduct of zinc, cadmium production worldwide is directly dependent upon the production and smelting of zinc ores. Canada, as the world's leading miner of zinc, also leads the world in mine production of cadmium. Hence, over 70 percent of the world's mine production of cadmium comes from Europe and North America, primarily Canada. While most of the cadmium-bearing zinc ore mined in the United States is smelted west of the Mississippi River, refined cadmium metal and its compounds, from both domestic and imported sources, is generally consumed east of the Mississippi.

Geology and Exploration

Zinc deposits containing cadmium occur within a variety of geological environments though in general the more economically important types of deposits fall within four broad categories. The most important type of deposits are those known as stratabound or Mississippi Valley type deposits. These deposits which may be found in districts covering hundreds of square miles are generally massive, flat lying, irregularly shaped bodies of zinc and cadmium sulfides which are scattered along favorable zones within certain carbonate rocks. The zinc deposits of the old Tri-State District of Missouri-Oklahoma-Kansas and those of central and eastern Tennessee are prime examples of stratabound deposits.

Other types of zinc-cadmium deposits of importance, though somewhat lesser commercial significance than the stratabound deposits, are the replacement deposits such as those mined at Bingham and Park City, Utah, the vein type deposits like those of the Coeur d'Alene District of Idaho and the lens-shaped stratiform deposits in metamorphic rocks such as those found in the Broken Hill and Mount Isa Districts of Australia. Exploration aimed at finding these various types of zinc deposits can be both expensive and time consuming and even under the best of conditions the rate of success is extremely low and becoming lower every year.

In order to illustrate the magnitude and complexity of some of the problems which must be faced during exploration, the following rather simplistic model is presented. For example, the shape, form, and relative position of stratabound ore bodies is difficult to describe without going beyond the scope of this paper. Imagine if you will, a multilayered chocolate chip cake in which only some of the layers contain chocolate chips and only some of the chips are real chocolate. The real chocolate chips in this case represent ore bodies and the nonchocolate chips represent subeconomic bodies of cadmium-zinc sulfides or other minerals. Further imagine being given the task of locating the chips present in each layer with the rules of the game being that the only tool you would be allowed to use would be a small thin-walled glass tube which you could insert into the cake but only through the top layer. Each time you probed or returned a core sample of the cake it could cost you $10,000 or $20,000 or more and if you were fortunate enough to spear through a chip, it may or may not prove to be the real chocolate which you were seeking. To make this illustration or model more realistic, the cake should be allowed to slide off the table and impact on the floor and thus reproduce the fractured and folded rock layers encountered in nature, then it should be covered with a thick green icing to represent soil and vegetation. Location and extraction of a real chip could ultimately return about 5 percent profit over and above the risk and expense of finding and recovering it.

Production and Consumption

The United States annually consumes about 12 million pounds or nearly 33 percent of the world's annual production of cadmium. Of this total, about one third is imported either in the form of refined metal or as a component of zinc concentrates or in flue dusts originating from zinc processing. About 75 percent of the concentrates which this country has received in recent years were imported from Canada and Mexico.

Cadmium, regardless of its market demand must be recovered at an early stage during the zinc smelting process. Early recovery is necessary both to avoid later interference by cadmium with the smelting or refining process and to prevent or reduce dispersal of cadmium via the zinc end. product, which for many applications must be as pure as possible.

The separation of cadmium from zinc at the smelter begins when concentrated ores from the mill are roasted to convert the zinc sulfide to oxide. The volatilized cadmium is collected as fumes or flue dust in baghouse collectors. The fume or flue dust may be further processed directly to produce cadmium metal. In electrolytic zinc plants the dust may be recombined with the roasted or sintered feed material, which is then taken into solution with sulfuric acid. A zinc-cadmium sludge is precipitated by adding zinc dust to the solution. The sludge is then processed to recover metallic cadmium by either the electrolytic or distillation methods of separation. The metallic cadmium is melted and cast into various commercial shapes such as balls, sticks or slabs.

The smelter recovery of cadmium from zinc ores on a worldwide basis average about 5 pounds of cadmium metal per 1000 pounds of recovered metallic zinc. As a result of this fairly constant relationship between zinc and cadmium any sustained reduction in the production of primary zinc due to smelter closures or lower capacity utilization for example, is ultimately reflected in the availability and price of cadmium supplies.

There are presently in the United States, six companies operating seven plants producing cadmium from domestic and imported ores. The value of this production in 1976 was over $17 million. The current producer price of cadmium is $3 per pound. However, over the past 20 years the price has fluctuated widely in the marketplace in response to supply and demand, technological changes, and general world economics.

As a result of numerous domestic smelter closures since 1969 for economic, technologic, or environmental reasons our reliance upon imported cadmium metal has climbed from below 10 percent to more than 60 percent of America's annual consumption. New zinc mines and additional zinc smelter capacity slated to come on stream in the near future should contribute to a moderate reduction in the volume of imported cadmium required to meet our industrial needs.

Reserves

Throughout the world the reserves of cadmium contained in known or currently recoverable zinc deposits amount to about 830,000 short tons of metal, 305,000 tons of which are contained in North American deposits. The total identified world resources of cadmium are estimated at over 20 million short tons; however, because of the low-grade of this material only a small percentage of this volume could be recovered using current technology.

Uses of Cadmium

In 1976 over 45 percent of the cadmium consumed in the United States was used in corrosion-resistant applications; 20 percent was used to produce various pigments; and the remaining 35 percent was consumed in alloys, plastic stabilizers, batteries, and other uses.

Conservation of natural resources such as petroleum and metals is one of the goals of the present administration. The National Commission on Materials Policy recently estimated that losses attributed to rusting and corrosion cost the nation roughly $15 billion, every year. No doubt this figure would be much higher if the use of corrosion-resistant coatings such as paint, resins, zinc, and cadmium, were restricted or severely limited. For certain corrosion-resistant applications cadmium plating is far superior to that afforded by zinc. Galvanized or zinc plated hardware when used in highly alkaline, marine and/or tropical environments quickly develops a weak, crumbly, surface coating composed of various zinc compounds. The bulky coating in turn tends to interfere with the movement and operation of intricate mechanisms. Cadmium, on the other hand, when exposed to similar environments develops a firm, thin, weathered surface free of undesirable deposits which provides protection equal to a coating of zinc 4 or 5 times as thick as the cadmium coating.

An illustration of the consideration that must be given to the use of substitutes is the use of cadmium plating on the clips which hold machine gun cartridges together as a belt. If these clips are painted or plated with zinc, for instance, 50 calibre machine guns used at sea, unless constantly maintained, would quickly jam as the products of oxidation interfered with the feeding and firing mechanisms.

Since cadmium is both highly conductive and easily soldered using noncorrosive fluxes cadmium plated components such as contacts and solid circuits are often employed in electrical and electronic devices, especially those which are to be exposed to marine or other severe environments.

The high ductility or stretchability of cadmium makes it extremely attractive for use in conjunction with metals which are to be formed by bending or die stamping. When cadmium plated sheet metal or flat stock is stamped or formed the thin ductile plating stretches and shrinks in concert with its base metal host without cracking around curves or otherwise separating from its substrate. One advantage to plating prior to forming is that it eliminates problems associated with cleaning and draining electrolyte from intricate or closed forms. Another is that plating coverage of uniform thickness can be maintained and assured throughout the end product.

In aircraft usage cadmium plating of steel fittings which will be in contact with aluminum is effective in overcoming a galvanic difference between the steel and aluminum. Eliminating the galvanic difference prevents corrosive failure of the metals at the point of contact.

Cadmium compounds are widely employed in the manufacture of pigments used in such products as paint, plastics, inks, and rubber. Colors such as yellow, orange, red, and maroon are prepared from cadmium compounds. Cadmium pigments extended by the addition of barium sulfate are known as lithopones and are widely used in the pigment industry. They are popular because of their excellent lightfastness or ability to withstand fading, darkening, dulling, or loss of hiding power after long exposure to light. Because of the toxicity of cadmium, cadmium-based pigments are not used in materials destined for use in food storage or handling, children's products, or products which come into direct contact with water supplies.

During the manufacture of plastics which are formed at high temperatures, cadmium compounds are added as stabilizers to minimize undesirable properties which would otherwise develop during the molding process. Toxicity of the end product is again a factor which is avoided where necessary by the use of more expensive and sometimes less effective cadmium-free stabilizers.

When combined in varying proportions with other metals cadmium forms a number of alloys ranging from tarnish resistant silver to metal which melts in boiling water. The latter, known as fusible alloy, is often used to pot or encapsulate oddly-shaped or delicate objects during the manufacturing process. For example, the flat end of aircraft turbine blades are mounted in a block of fusible alloy which can then be clamped to the machine which cuts and finishes the dovetailed end by which the blade is attached to the turbine rotor. When machining is complete the blade and alloy are placed in boiling water where the alloy melts away from the finished blade. The fusible alloy is entirely reclaimed and used again for later potting operations.

The addition of up to 1 percent cadmium to copper increased the tensile strength of copper wire and enhances its resistance to wear caused by sparking and abrasion which may occur in overhead wires such as those used by trolleybuses and electric railways.

Other cadmium alloys are employed in nuclear reactor control rods, bearings, and special purpose solders. Cadmium was at one time combined with mercury, another toxic substance, for use as a dental amalgam which, fortunately for the dentist and patient alike, is no longer in use.

The rapidly expanding use of cadmium in nickel-cadmium batteries and cadmium sulfide solar cells may offset the decline in consumption of cadmium for dissipative uses, resulting from the change to alternative materials. In addition to the use of cadmium in the small, increasingly popular rechargeable ni-cad batteries which are available for flashlights, pocket calculators, and other consumer electronic goods. A positive aspect of these new applications is that recycling of discarded products can be encouraged and implemented through a system of returnable deposits and/or obsolescence promoted via improved technology.

The average growth rate for cadmium consumption between now and the end of the century is estimated to be on the order of about 2.7 percent per year for the United States and 3 percent per year for the rest of the world. In the United States storage batteries, plastics, and synthetics are forecast to be the major areas of cadmium consumption. The total annual world consumption in the year 2000 is expected to amount to about 41,000 short tons compared with nearly 19,000 short tons in 1976. Assuming that the supply/demand trends established for both cadmium and zinc over the past 20 years remain valid, then the supply of cadmium available for industrial usage worldwide should be more than adequate to meet all requirements.

Environmental and Strategic Considerations

Cadmium is distributed throughout our environment as a result of the breakdown and exposure by weathering of cadmium-bearing rocks and minerals. Consequently, the soils of some areas may contain naturally high (eg. 0.01 percent cadmium, East Tennessee) concentrations of cadmium while the soils of other areas may not.

Natural contaminants of one sort or another abound in nature and like the uncontrollable ecological disasters frequently caused by forest fires, floods, and volcanic eruptions there is little that can be done to avoid some contamination. The industrial dispersal of cadmium into the environment has for some time been recognized as a cause for concern by both government and by the industries involved in its production and usage. This concern has been translated into a notable reduction of cadmium emissions to the environment from a multitude of controllable sources.

The recent interest in the use of substitutes for cadmium is being intensified not only from the standpoint of attempting to reduce further those emissions of cadmium which are due to its dissipative uses, but also to assure that in the event of a national emergency, which might curtail imports of metals of all sorts, that adequate substitute materials will be available and ready to meet certain strategic applications without long delays due to testing and evaluation.

In the interest of brevity only the most salient technical features related to cadmium have been presented here today. One of the many activities of the U.S. Bureau of Mines is to assemble and disseminate economic, and technical data on the supply/demand relationships of about 100 commodities, including cadmium. The Bureau regularly publishes numerous comprehensive technical reports designed to help both government and industry to keep abreast of the ever-changing status of national and international mineral resources. Its publications include the Minerals Yearbook, Mineral Facts and Problems, the Mineral Industry Surveys series and many specialized reports dealing with current events of mineral commodities. For those of you who may be interested in two of our recent publications dealing with cadmium I have a limited number available here for distribution. I have here also a number of forms which may be used to order various Bureau of Mines commodity reports, including those pertaining to cadmium.

Selected Bureau of Mines Publications

Mineral Industry Surveys, "Cadmium"
Published quarterly and annually.

Bureau of Mines Minerals Yearbook,
"Cadmium," 1975 preprint.

Mineral Facts and Problems,
"Cadmium," 1975 preprint.

Commodity Data Summaries 1977

Mineral Trade Notes

Mineral Trends and Forecasts, 1976

Status of the Mineral Industries, 1977

Minerals & Materials/A Monthly Survey

Minerals in the U.S. Economy, 1977

These and other publications are available from:

Division of Technical Reports
Office of Mineral Information
Bureau of Mines
U.S. Department of the Interior
2401 E Street, NW.
Washington, D.C. 20241

or

The Branch of Publication Distribution
U.S. Bureau of Mines
4800 Forbes Avenue
Pittsburgh, Pa. 15213

Evaluation of Alternatives

Session V

Thursday Morning 10:05

REPLACEMENT OF CADMIUM ELECTROPLATING ON IBM HARDWARE

Allen W. Grobin, Jr.
IBM Corporation
Pouch Keepsie, New York 12602

The paper briefly describes IBM's efforts, initiated in 1973, to identify and replace cadmium electroplated hardware parts.

Types of electroplating are identified on part drawings by code numbers. Through the use of a corporate central file records system, approximately 2 million part drawings were search by computer. The search identified approximately 2500 parts that were electroplated with cadmium. These parts were further sorted by application or function as well as engineering group of control.

Of these 2500 parts, only 60 were electroplated with cadmium for the metallurgical properties of cadmium. The rest merely required corrosion protection.

Parts requiring corrosion protection were changed to zinc electroplating. Parts requiring lubricity for sliding action were evaluated using zinc electroplating and a water-emulsion wax post treatment and electroless nickel. Parts requiring solderability were evaluated with tin and tin-lead alloys. The description of the code number representing cadmium electroplating was changed to zinc and only those parts requiring tin or electroless nickel electroplating required an engineering change.

REPLACEMENT OF CADMIUM ELECTROPLATING ON IBM HARDWARE

A. W. Grobin, Jr.
International Business Machines Corporation
Poughkeepsie, New York 12602

This paper describes the sequence of events, the mechanisms, and procedures that were used by IBM in the orderly replacement of cadmium electroplated parts. It also draws parallels for the handling of similar concerns such as energy conservation and material shortages.

The IBM Poughkeepsie facility had technical responsibility for electrodeposited coating and related finishes for the corporation. In February 1973, the Materials Laboratory at Poughkeepsie was notified by the IBM manufacturing facility in Fujisawa, Japan that the Japanese government was about to place severe restrictions on the production and use of cadmium electroplate. Consequently, the identification of cadmium coated parts became necessary.

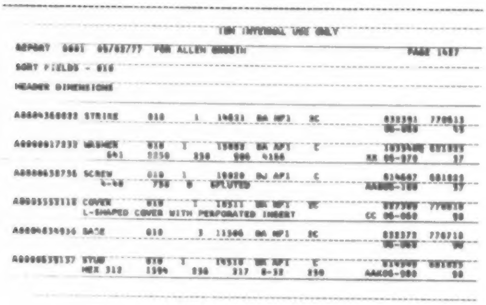
Telephone communication with Japan made us fully aware of the environmental problem in and around Toyama Prefecture and of the so-called Itai-itai disease and brought to focus the potential magnitude of the problem on a world-wide basis. This problem had apparently been brought about by increased production and by faulty treatment of waste water from the Hamioka cadmium mine during World War II. Polluted water from the Jintsu River was used to irrigate the rice fields. Shellfish at the mouth of the river were also contaminated. Thus cadmium entered the food chain and the drinking water. It appeared that governmental authorities, in an effort to remedy the situation, were going to set standards for cadmium in effluent that went beyond the capability of the small job shop electroplater. Cadmium electroplating would have to be carried out in completely new facilities designed to meet these proposed standards. This would, of course, make the electroplating of cadmium impractical, if not impossible, in the local job shops where the bulk of metal finishing work is done.

With the growing world-wide awareness of the need for pollution control, it was reasonable to expect a number of other countries to follow the lead set by the government of Japan. We therefore included in our planning for the solution of the immediate problem the premise that cadmium electroplating would become unavailable except under priority conditions.

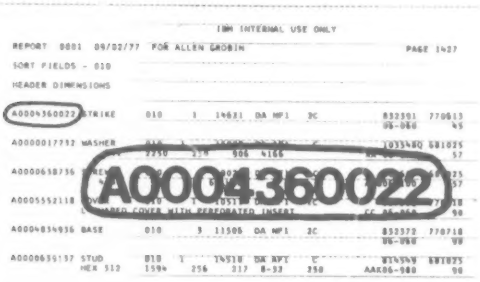
At the time, IBM had about two and one-half million active part numbers being used in the product line and being manufactured in fifty U.S. and foreign plants. Engineering control was the responsibility of a dozen development laboratories. Keeping track of these parts and their use is the function of the corporate central file. This is a unique computerized file that records and updates all the vital information for each part, including laboratory of control and using manufacturing sites. Also included is the raw material, finish, and a description of the part based on key dimensional or functional parameters. The information about each part is in the form of code numbers. These code numbers are used to call out material and finish on each part drawing. Suppliers are furnished with a regularly updated booklet which defines these code numbers.

The latest edition of the IBM supplier guide, "IBM Materials, Finishes and Processes," was published in January 1977. The booklet is issued under the IBM standardization program as C-P 0-0205-001 and is sent to all of our suppliers, fabricators, and subcontractors. The latest specification covering the material or finish is identified.

A detailed description of the central file can be found in Fred Groppuso, "How IBM Computerized Its Control System for More than Two Million Machine Parts," Computers and Automation, September 1973, and reprinted in Standards Engineering, February 1974.

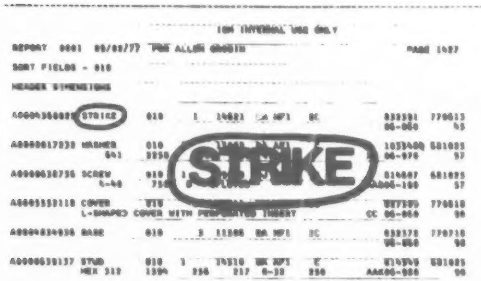


To investigate the use of cadmium, a routine inquiry was made to the central file requesting a listing of all part numbers using any of several cadmium finishing codes. Here is a page from a recent central file report. The report form is flexible and can be tailored to the user's needs. In addition to storing information on materials and finishes, the file contains physical dimensions, laboratory of engineering control, manufacturing sites using the part, and sources, to name a few records.

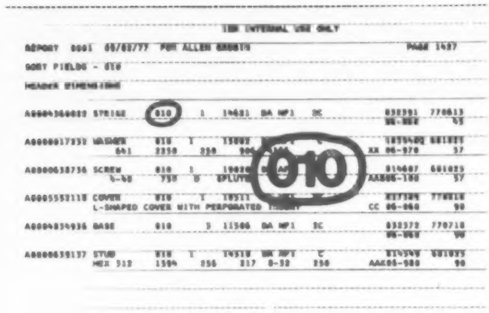


```
                         IBM INTERNAL USE ONLY
REPORT  0001  09/02/77  FOR ALLEN GROBIN                         PAGE 1427
SORT FIELDS - 010
HEADER DIMENSIONS
A0004360022 STRIKE     010     1  14621  DA MF1   2C              832391  770613
                                                                  06-060      45
A0000017732 WASHER     [illegible]                                1035480 681025
                       2250    [illegible]  906  4166             [illegible] 57
A0000638736 [illegible]
A0005552118 [illegible]
            [illegible] COVER WITH PERFORATED INSERT              CC 06-060   90
A0004834936 BASE       010     3  11506  DA MF1   2C              832372  770718
                                                                  06-060      90
A0000639137 STUD       010  1     14510  DA AF1   C               814549  681025
            HEX 512    1594   256    217  8-32    250          AAK06-980      90
```

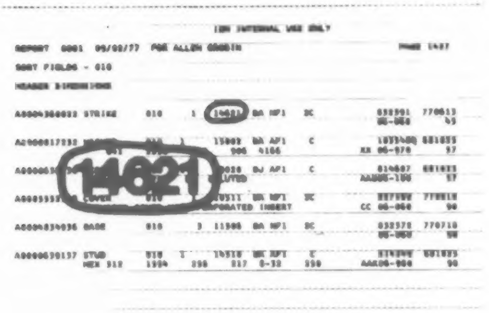
The part number is shown in column one. Included elsewhere in the printout are codes that indicate whether the number is for a detail part or assembly and whether it has an active, obsolete, or field replacement status.



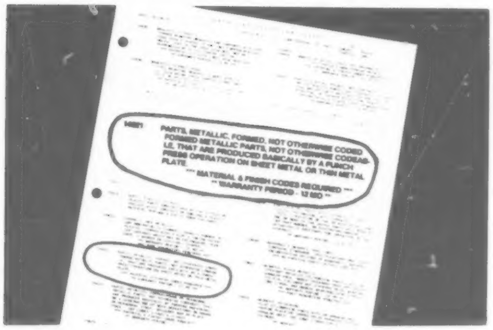
The second column is a one-word part name.


IBM INTERNAL USE ONLY
010

This is the code for the laboratory of engineering control. The controlling group is responsible for all changes to the part. All IBM parts are available for multiple use. A new user of a part establishes usage through the records system and is thereafter consulted by the laboratory of engineering control prior to any change.

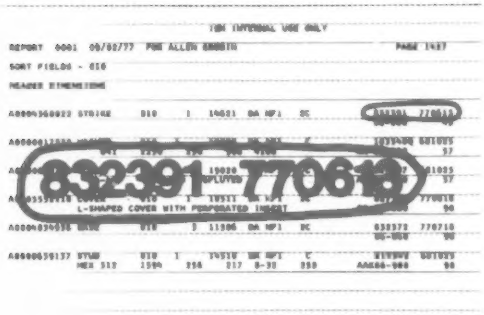

IBM INTERNAL USE ONLY
14621

The data classification number appears next. This code identifies groups of similar parts. This number has a variety of uses such as searching existing parts for application in a new design or determining the part function without seeing the actual drawing.

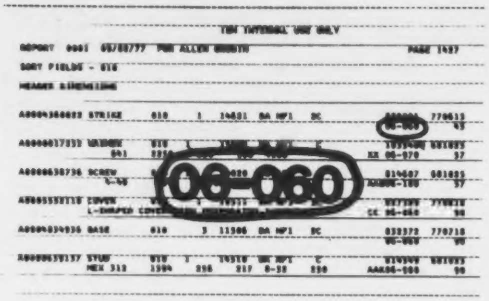


14621 PARTS, METALLIC, FORMED, NOT OTHERWISE CODED
FORMED METALLIC PARTS, NOT OTHERWISE CODEABLE, THAT ARE PRODUCED BASICALLY BY A PUNCH PRESS OPERATION ON SHEET METAL OR THIN METAL PLATE.
*** MATERIAL & FINISH CODES REQUIRED ***
** WARRANTY PERIOD - 12 MO **

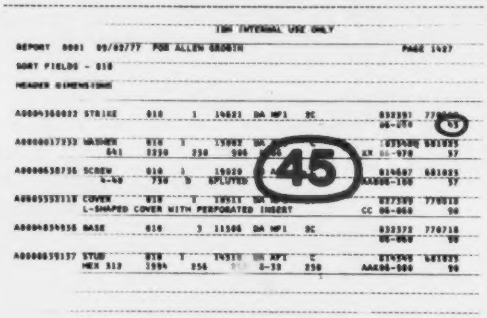
This is a page from the "IBM Data Classification Manual," highlighting the description of code 14-621.


IBM INTERNAL USE ONLY
832391 770613

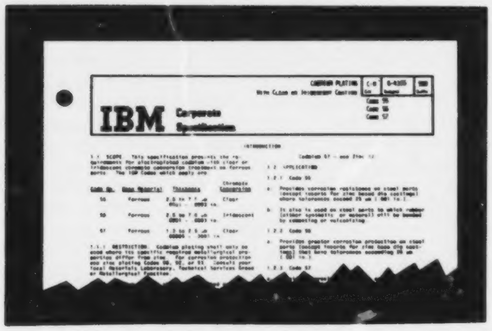
Indicated here on the central file report is the current engineering change level number and its data.



The code number used on the drawing to represent the base material is next. In this case, the code 06-060 represents AISI 1010 steel in tempers 1 through 5.



The last column shows the code used to define the finish. Finish code number 45 represents hard chromium electroplating.



The IBM supplier guide will direct the supplier to IBM specification C-H 6-4104-500 for the requirements of the finish. The use of code numbers instead of actual materials and finishes allows for economical changes to drawings as well as providing a rapid assessment of usage and application.

The complete printout was received by mail in three days. Optionally, it could have been transmitted via telephone line and terminal printer. An analysis of the printout showed that 35 manufacturing sites used cadmium electroplating for machine parts either in house or at a job shop. The total number of parts involved was about 2500. An examination of the data classification code number very rapidly showed that most of the parts were electroplated for corrosion protection, but only about 60 parts required detailed examination to determine why cadmium was specified.

Only six sites were involved with engineering control of the sixty parts.

The controlling engineering groups were notified that these parts should be changed from cadmium to some other finish. The materials laboratory at every site was notified that no new parts could be released with a cadmium finish unless there was no alternative. The bulk of the parts plated with cadmium were simply and automatically changed to the corresponding zinc electroplating by changing the description of the code number from cadmium to zinc. This technique of changing the description of the code number used to describe a material or finish on a part drawing provides an inexpensive means of making extensive changes. This wholesale change was not without its problems; the few problem parts became evident very rapidly.

For example, some cast iron and nitrided parts could not be adequately covered in the standard zinc cyanide bath. However, adequate coverage was obtained by use of noncyanide zinc plating baths.

Replacement electroplatings were found and tested for the 60 parts that had required the functional properties of cadmium. For sliding wear, the substitute was autocatalytic nickel, hard chromium, or a dry-film lubricant such as electrodeposited molybdenum disulfide. In one case the base material was changed from steel to aluminum and the surface anodized with a codeposit of TFE. Where solderability was a factor, tin electroplating was substituted.

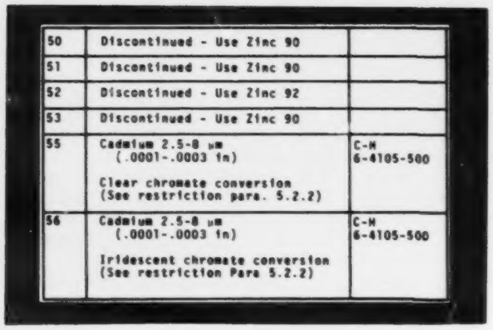
Previous corrosion studies showed that zinc was equal to, or better than, cadmium for our applications. Therefore, the wholesale switch from cadmium to zinc for the bulk of the parts where corrosion protection was the objective could be made.

In September 1973, after all testing of replacement finishes for cadmium was completed, a revised specification for the three cadmium electroplating code numbers used on drawings was issued. This document had the two following special clauses: "RESTRICTION. Cadmium plating shall only be used where its specific required metallurgical properties differ from zinc. For corrosion protection use zinc plating Codes 90, 92, or 93. Consult your local Materials Laboratory, Technical Services Group or Metallurgical Function." and "EXISTING DRAWINGS. After 1 January 1974, IBM part drawings calling out cadmium plating will be plated in zinc according to the schedule below unless a note on the drawing states a metallurgical need for cadmium.

Cadmium 55 - use Zinc 90
Cadmium 56 - use Zinc 93
Cadmium 57 - use Zinc 92"

The materials and finishes guide for suppliers carries the restriction and existing drawing notice in each edition.

Today, of the approximately 100,000 parts that are subject to a metal finishing operation, no more than a dozen parts require cadmium finish. Other finishes with the functional properties of cadmium are in use. We have learned to design without a dependence on cadmium.



50	Discontinued - Use Zinc 90	
51	Discontinued - Use Zinc 90	
52	Discontinued - Use Zinc 92	
53	Discontinued - Use Zinc 90	
55	Cadmium 2.5-8 µm (.0001-.0003 in) Clear chromate conversion (See restriction para. 5.2.2)	C-M 6-4105-500
56	Cadmium 2.5-8 µm (.0001-.0003 in) Iridescent chromate conversion (See restriction Para 5.2.2)	C-M 6-4105-500

This does not mean that our parts are totally free of cadmium. In some instances, commercial items and assemblies are available only with cadmium electroplating. Where possible, we have had the finish of these items changed. However, the bulk of these items are finished to a federal or military specification and our small volume cannot justify a second finishing operation by the manufacturer.

Our studies have shown that zinc more than adequately protects our parts from corrosion and, in fact, with the advent of the cyanide-free zinc baths the protection exceeds that of cadmium with an added overall cost reduction.

The cadmium situation is not unique. Materials generally are coming under greater scrutiny, not only from the standpoint of toxicity and flammability, but also from the concern of availability. Added to these concerns are energy conservation, productivity, and cost reduction. More and more we are going to need to identify what we are using, where we are using it, and how much we are using.

I have attempted to show that what might have been a very difficult, time consuming and expensive task was accomplished easily and quickly and, in fact, produced a net cost savings through the use of automated computer control of part drawings.

Our use of codes on drawings to represent materials and finishes combined with our method of codifying part drawings allows our record system to compile a where-used trace for materials and finishes. In addition, the automated record system allows for multiple use of parts and single sourcing for multiple plant usage, thereby providing economic advantage in fabrication, finishing, waste treatment, and energy consumption.

Replacement of Cadmium Electroplating on IBM Hardware

Discussion Period

MR. HRATKO: Bill Hratko, Sundstrand. When you substituted zinc for cadmium, did you find that the corrosion resistant properties were equivalent, or did you have to compensate by plating more zinc versus cad?

MR. GROBIN: We didn't have to compensate. You have to look at the application of the part. It has been brought out that zinc protects better than cadmium in industrial environments which have a higher sulfide contaminant level. We found that direct substitution actually improved the resistance.

I noted in personally examining a number of parts at test sites that the corrosion on cadmium was far greater than the corrosion on zinc for equal thicknesses and equal conversion coating.

MR. JORCZYK: Ed Jorczyk, 3M Company. Do you specify the type of bath the zinc shall be plated in?

MR. GROBIN: No, we do not. We feel that it is much better to specify the end requirement and allow the finisher to use whatever innovative techniques are available to him to provide us the best quality at the most economical price. We review his process before we accept it, but we allow the supplier to use all the metal techniques and knowledge at his command. We feel that the metal finisher is a highly skilled, very technically oriented person who is quite capable of managing the finishing operation. We come to an agreement with him on the finishing operation, but we allow him as much latitude as possible.

MR. COOK: Albert Cook, ILZRO. Could you go into more detail about the dozen parts which are still being cadmium plated?

MR. GROBIN: I only talk about a few of them and they primarily had problems with adhesive bonds. As pointed out in one of the previous papers, it is very difficult to get good adhesive bonding to zinc electroplating while cadmium electroplating gives very good adhesive bonding. We are still looking at the problem, looking at new adhesives. We are looking at some of the individual zinc electroplating and zinc coatings. We want to include mechanical coating. We do use them; we have specifications to cover them.

There appear to be some differences in properties in the various zincs. In ASTM Committee B-8, we are going to be testing the differences in types of zincs to see if that situation is real or not.

MR. CLANTON: Jim Clanton, RCA, Camden, New Jersey. Mr. Grobin, Did you state that you realized the importance of this problem in 1973?

MR. GROBIN: Yes.

MR. CLANTON: You made a major turn around in four years and it is amazing how you replaced cadmium in a lot of applications. Without some major history of tests, were you faced with any major problems?

MR. GROBIN: Sure. We did it in approximately five months. We issued the specifications in September of 1973, and they went into force January 1, 1974. We have been regularly in production since that time. Each laboratory got that specification as it was published. They immediately became aware of the parts that they had under their control. They had equal access to the file. They went to the file and asked for all the part numbers that were plated in cadmium. They looked at them to see what their logistics problems were going to be and immediately started locating zinc electroplaters to handle the switch over, and notifying the cadmium electroplaters that they were going to stop plating in cadmium. They looked for parts which might present a difficulty. I mentioned a few, such as the cast iron parts and the carbonitrided parts.

My office was asked what to do on those parts which couldn't be plated in zinc. We located a company that had developed a new noncyanide zinc bath, and we bought a quantity for evaluation. They also informed us that other people were using the bath and had been satisfied with it. Our test results showed that the bath lived up to everything that they stated. Indeed, it plated on cast iron parts, and it actually did a better job than cadmium.

One benefit was a lower rejection rate of parts. We found that more attention had to be paid to the cleaning of the part. You know, cadmium is very easy to electroplate. I would swear you could plate cadmium on paper if you tried it. That is the one thing that got cadmium really going. Unfortunately, cadmium will plate over poorly prepared surfaces and they will creep through into the product. But on the zinc plated parts, this is not so. Your bad parts come out, and your plater has to be more careful in his preparation cycle.

MR. CLANTON: Were military contracts treated in a similar manner?

MR. GROBIN: No. Military contracts are executed to everyone on the same basis. IBM has no different treatment. When the government issues us a contract, we plate it according to the government's specifications. If they want cadmium on it, we put cadmium on it.

MR. HOVEY: Ralph Hovey. At Amphenol we have not been as fortunate as you. We have tried zinc on some products, and, from our lab testing, there was a beautiful change, but our customers, being electronics people, invariably run their systems through freon. Zinc just doesn't tolerate freon, and freon does not tolerate zinc. The two are incompatible. One of the big notes on all freon equipment instructions is that under no circumstances zinc should enter into these solution. You can imagine what happens to electronic equipment when zinc is put on it. With out our knowledge, our customers used freon in their cleaning systems prior to soldering and other processes.

This meant that where we had used zinc, we had to very carefully evaluate everything, assuming that the customer was going to use a freon degreasing. There are a lot of little things that are not immediately obvious to people. You have to find out what your customer is going to do with the plated product before you can get home clean and free.

MR. GROBIN: That is right. We had a similar problem, and primarily used tin electroplating. We used tin in a number of ways: We used tin plating by itself, tin over nickel plating, a tinzinc plating, and tinlead.

MR. GORDON: Phil Gordon, CulterHammer. The impression you have left is that in this changeover the bulk of the replacement of cadmium with zinc was based on considered engineering judgment. I think the question was directed at how much evaluation and testing after the fact, or perhaps you had it as a history before the fact, was involved in this particular aspect? To what extent was your judgment right, and where did you have to pull in your horns and turn around?

MR. GROBIN: There was a very intensive effort between February and September in evaluating the parts. As you can imagine, there are many people who, when they hear a change, will scream loud and long. We put this out as being a directive and remaining in cadmium had to be justified, meaning that the person who really had a problem had to prove it.

It is not hard to prove that you have a problem. If you have a part that will not work because of being changed to a zinc electroplating, you can demonstrate that. But if you are talking about a bracket fastener that is going to be used to hold a switch onto the frame of a computer, it is going to be very difficult to justify staying in cadmium for corrosion protection. Primarily, our parts are coated for corrosion protection.

As I indicated here, 2500 parts in cadmium and only 60 of them were using functional properties, or appeared to be using functional properties, of cadmium. So primarily, our parts are plated for corrosion protection.

MR. ZEHNDER: Joe Zehnder, Enthone, New Haven, Connecticut. I can appreciate IBM's concern with pollution of the environment due to cadmium electroplate, but has any attempt been made to reduce this pollution by reduction of cadmium pigments or nickel cadmium batteries?

MR. GROBIN: I really can't answer that because I don't know what pigments are used in our paints. We have a requirement that our paints be non-toxic so I doubt that cadmium pigments are used in them, but I can't state that definitely. As far as nickel cadmium batteries are concerned, that area is handled by someone else who has a responsibility similar to mine and I don't know what he has done.

MR. ZEHNDER: It seems as though the electroplater is bearing the brunt of cadmium pollution. According to the data we were given the other day, 54 percent of the cadmium consumed is used in electroplating. I just wonder if anyone has any data showing what percentage of the pollution is due to uses of cadmium other than electroplating.

MR. GROBIN: I think you have a very good point. It would probably be better brought up at the Panel discussion this afternoon.

MR. PON: My name is Kee Pon. I'm with the Naval Ship Engineering Center. Earlier you mentioned that when you supply hardware to the military, you follow military specifications. Bear in mind, many of the specifications are old and the specifications are normally prepared to suit what is available. In the case where you have already trimlined to use something else, I think it is an easy test just to inform your procurement agency that new substitutes are available and that it would be to the government's benefit to use the new ones. Normally such requests are granted where justified.

MR. GROBIN: We are aware of that. Sometimes that works and sometimes it doesn't. It is a problem of the government having policies and individuals to carry out these policies. Some people are more reasonable than others.

MR. WHITE: Marty White, Cadmium Association. You say this replacement from cadmium to zinc was started by reports that the Japanese government was going to introduce very stringent control measures. Out of the 2500 parts that were cadmium plated, how many were plated in Japan?

MR. GROBIN: The actual number that were plated in Japan was several hundred. I don't recall the exact number. Primarily, they were fasteners and brackets. They were used in large quantities so while the number was perhaps 200, the volume would be rather high.

MR. WHITE: But you didn't contemplate just changing those particular ones to zinc? I am thinking of the cost. You seem to react very quickly to something that was happening several thousand miles away. Some of your U.K. factories were very upset about your change from zinc to cadmium because of pressures that were not affecting them in the slightest.

MR. GROBIN: Yes. They always seem to be upset with everything I do. I spend more time going to the U.K. than to any other country because of that.

MR. COOK: Albert Cook of ILZRO. It seems to me that IBM is fortunate in this respect. On the one hand your corrosive environment is not as severe as some, and on the other hand, your choice of alternatives of zinc plating has been extremely well documented. You have plenty of data available on zinc plating. Could you comment a little more on the sort of corrosive environment that you normally meet and how you feel about going to other than zinc plating for use in a marine environment?

MR. GROBIN: We actually go into marine environments. We go into every type of environment in this world. Our product is sold all over the world. We find that the greatest usage is obviously in the industrialized nations. Various reports will show that the industrialized nations are the greatest consumers of energy, and among the byproducts of consuming energy are sulfur dioxide and hydrogen sulfide. So these atmospheres are prevalent.

I think it was pointed out yesterday that operational aircraft on aircraft carriers are having problems from the sulfur dioxide coming from the stacks of the oil being burned to run the ship. The sulfur dioxide problem is worldwide, while salt corrosion is not. These problems have to be taken care of.

I think some of the new alloys that we are seeing probably will end up being the answer. But that is only a guess on my part. I don't think that we will ever get rid of cadmium for electroplating completely. I think it serves some very vital functions. I believe it is overused. I don't see any new thinking or very much new thinking in the area. Designers seem to use what they used last year. I think we have to get back to the designers and tell them that it is their mission to start looking at new materials. It is up to them to start the initiation of using these things and having them tested and evaluated.

Thursday Morning 10:40

EVALUATION OF COATED FASTENERS: ALTERNATIVES TO CADMIUM PLATING

Howard J. Dolejs and Raymond E. Geisert
Gould Inc. Ocean Systems Division
Cleveland, Ohio 44117

A variety of coatings for steel fasteners are being evaluated as alternatives for cadmium plating for improved corrosion resistance. The requirements for the coatings are that they withstand a variety of corrosive environments and be compatible with the aluminum alloys. Also, the application process should not affect the base metal properties of the fastener. Other fastener coatings such as black oxide and mechanically applied cadmium offer less corrosion resistance than electroplated cadmium. The six types of vendor applied coatings evaluated consisted of electroplated aluminum, IVD aluminum, thermal decomposition aluminum, chrome-zinc plating, diffused nickel cadmium, and baked polymer over cadmium plating. The coated fasteners were tested per MIL Standard 1312 for hardness and stress durability and were exposed to a 5% salt spray to failure or 45 days, whichever came first. Potential measurements of the various coatings were made and compared to 7039 aluminum alloy which is used for the torpedo shells. Environmental tests in the engine exhaust and in Otto Fuel/sea water vapors are in progress. The galvanic current generated by each type of fastener coating when connected to 7039 aluminum alloy is being measured. Results to date show that only the polymer coated cadmium plating meets the requirements. Other tests are in progress.

Reproduced from
best available copy.

EVALUATION OF COATED FASTENERS
ALTERNATIVES TO CADMIUM PLATING

by

H. J. Dolejs and R. E. Geisert

Gould Inc. Ocean Systems Div.
18901 Euclid Ave.
Cleveland, OH. 44117

INTRODUCTION

A variety of threaded fasteners are used in the underwater systems designed and manufactured by Gould Inc. These underwater systems are of modular construction and are typically made up of several separate aluminum alloy sections. The sections house the electronics, and propulsion sub-systems and are also used for fuel tanks. The modular construction allows for ease of assembly and disassembly, testing, maintenance and change in configuration from practice to warshot condition.

The majority of the fasteners are cadmium plated with a chromate conversion coating. Other fasteners have a black oxide coating. All are either MS or NAS aircraft quality type socket head cap screws or custom machined to Gould design. The sizes range from 4-40 to 9/16-18. During sea trials and in storage the fasteners are exposed to a variety of corrosive environments including:

a. seawater
b. fuel and seawater, both liquid and vapor
c. high temperatures
d. combustion products - cyanides, acids, and reducing gases

The cadmium plated fasteners are exposed to all these environments and black oxide coated fasteners to only the latter two. Cadmium plated fasteners are also used on electronic components within protected environments.

A company funded research program was initiated to find coatings with better corrosion resistance than the ones presently used. Black oxide coatings corrode rapidly. Cadmium plating lasts longer, but may corrode after two or three sea runs in the practice units. Acceptable parameters for a new coating(s) were:

a. Better corrosion resistance than electroplated cadmium.

b. Application of coating must not affect the base metal properties of the fasteners, no hydrogen embrittlement and no loss of mechanical strength.
c. Compatibility from a dissimilar metal stand point with the aluminum alloys in the system. NOTE: One alloy used is 7039, an aluminum-magnesium-zinc alloy that is one of the more anodic aluminum alloys. Its corrosion potential approaches that of zinc.

A review of reports on fastener coatings and trade literature was made to select promising coatings. One report surveyed various coatings for the harsh environment of aircraft carrier catapults [ref (1)]. The Air Force and NAVAIR were also interested in aluminum coatings for high performance aircraft [ref (2)]. A fastener manufacturer related that a diffused nickel cadmium coating was being used by some aircraft manufacturers. Other coatings mentioned in trade literature, were proprietary polymer coating and a chromium zinc flake coating that is used in the automotive industry. The program was established to evaluate these types of coatings.

Cadmium coatings other than electroplated had been examined briefly, but were not included in the program. It was found that mechanically applied cadmium did not afford the desired corrosion protection, nor could it be sucessfully applied to the fine threads of the smaller fasteners. Vacuum cadmium, did withstand the salt spray corrosion test, but did not offer significant improvement over electroplated cadmium. Emphasis was placed on coatings that would offer clear advantages over electroplated cadmium.

TEST PROCEDURE

Procurement of Fasteners

To facilitate the use of the test fasteners in future sea runs, a standard fastener size MS 16998-29 (10-32 x 3/4" socket head cap screws), except without plating, was selected. However, it was discovered that plain, uncoated high tensile strength fasteners were difficult to obtain. Eventually one thousand unplated fasteners were purchased; unfortunately they were all coated with a black scale produced by a quenching operation. To remove this scale prior to coating, and without introducing hydrogen embrittlement, the screws were cleaned mechanically by fine abrasive blasting.

Application for Protective Coatings

After cleaning, lots of 50 fasteners were sent to selected vendors for coating with their specialty coatings. The types of vendor-applied coatings evaluated consisted of electroplated aluminum (0.3 mil), IVD aluminum (0.3 - 0.5 mils), thermal decomposition aluminum, chromium-zinc flake coating, diffused nickel cadmium (AMS 2416), and baked polymer over cadmium and over chromate coated IVD aluminum. Additional protective coatings such as chemical conversion (chromate) coatings per MIL-C-5541 and/or a proprietary silicone polymer coating were applied to aluminum coated fasteners by Gould.

Testing of Coated Fasteners

The coated fasteners were tested per MIL-STD-1312 [ref (3)] for Hardness (test no. 6), Stress Durability (test no. 5), and Corrosion Resistance (test no. 1). The corrosion resistance test which consisted of exposure to a 5% salt spray, was continued until the test samples either failed or until an arbitrary 45 day test limit had been reached. All incoming lots of production fasteners are routinely subjected to these tests, except that the salt spray requirement is 96 hours.

Since standard fasteners that are used in marine vehicles are often exposed to fuels, seawater and their vapors, as well as to combustion product environments, the experimental test fasteners were also exposed to these atmospheres under controlled laboratory conditions and in a propulsion test stand run.

Accelerated corrosion can occur when dissimilar metals are electrically coupled and exposed to a corrosive environment. In galvanic corrosion, the active (anodic) member will corrode in preference to the noble (cathodic) member. The galvanic series which is based on difference of corrosion potential, indicates if galvanic corrosion could occur. The current generated by a dissimilar metal couple is a measure of the rate of corrosion. To determine compatability, corrosion potential measurements were made on each of the coated fasteners and 7039 aluminum in synthetic seawater (ASTM 1142). The galvanic current generated by the fastener coatings and 7039 aluminum was also measured.

Environmental Tests

The coated fasteners were subjected to the total environments they would encounter in actual use. Six fasteners with the various coatings were installed in 6061-T6 aluminum blocks and torqued to 50 inch pounds, the normal installation torque. A light coating of petrolatum was used as a lubricant on the aluminum coated fasteners, because there was slight tendency to gall with the aluminum block. The test was run in duplicate. The two blocks were mounted in a static test fixture and subjected to a total of 54 minutes of propulsion operation. In this test, the environment consisted of high temperature, and propulsion exhaust products. After the runs, one of the blocks was then subjected to a 24 hour salt spray exposure to determine the amount of corrosion protection remaining.

In another test, the coated fasteners were exposed to fuel and seawater. Since the fuel is more dense than water and insoluble, there was a layer of seawater on top of the fuel. The fasteners were suspended in both liquid layers and exposed for one week at 140°F.

This was followed by exposure to the vapors above the liquids for one week at 140°F. It had been found that the fuel/seawater vapors were particularly corrosive. In addition to the other fasteners, this test included IVD coated fasteners with a chromate conversion coating, and the baked polymer coating previously mentioned. Of the IVD coatings only the 0.5 mil coating was exposed in this test.

Electrochemical Tests

Potential measurements were made on the coated fasteners and compared to 7039 aluminum alloy. Wire leads were soldered to the threaded end of the fastener and then a plastic tube was pushed over the wire and the fastener to isolate the solder connection from the synthetic seawater electrolyte.

The six fasteners with the various coatings and a 7039 aluminum alloy specimen were installed in the top of a versatile polarization cell using teflon adaptors. [ref (4)]. The top has nine threaded holes so that each specimen would be isolated yet exposed to the same electrolyte. Potential measurements were made using a Keithly model 616 Digital Electrometer with a Saturated Calomel Electrode (SCE) as the reference electrode. These measurements were made daily over a period of four weeks.

Galvanic current generated by the more promising coatings and 7039 aluminum were measured using the zero resistance ammeter (ZRA) technique [ref (5)]. In this test the specimens were connected to a potentiostat set at zero volts. The corrosion current was measured over a 24 hour period using a highly accurate current meter.

Standard Tests

The following tests were performed on all coated fasteners in this program.

Hardness Test (MIL-STD-1312, test no. 6)

Five screws selected at random from each coated fastener lot (type) were subjected to a hardness test conducted in accordance with MIL-STD-1312, test no. 6. Prior to testing, the sample screws were embedded in epoxy resin in a metallurgical mount, sectioned, and polished to provide a stable flat surface for the test. The hardness measurements were made on a Rockwell Hardness Tester.

Stress Durability (MIL-STD-1312, test no. 5)

Four screws selected at random from each coated fastener lot (type) were subjected to a stress durability test conducted in accordance with MIL-STD-1312, test no. 5. The sample screws were first coated with a graphite filled lubricant conforming to MIL-T-5544, and then threaded into a tempered, test block and torqued to a predetermined value which would produce a tensile stress on each screw equal to 75% of the minimum ultimate tensile strength of the fasteners. Since all of the fasteners were of the same size, per MS 16998-29, the torque value was 50 inch-pounds which produced a tensile load of 2380 pounds, as determined on a Skidmore Wilhelm Torque/Tension Tester. This represents 75% of 160,000 psi min. tensile strength.

After mounting, the screws were allowed to remain undisturbed at room temperature for 200 hours and then were removed from the test block, cleaned with solvent, and inspected for cracks and other anomalies.

Corrosion Resistance (MIL-STD-1312, test no. 1)

Five screws selected at random from each coated fastener lot (type) were subjected to a corrosion resistance test conducted in accordance with MIL-STD-1312, test no. 1. This test consisted of suspending the fasteners in a standard rubber lined salt spray chamber (as described in ASTM-B-117-61) and exposing them to a continuous salt spray (5%) until failure occurred or until an arbitrary 45 day test period had expired, whichever came first. After termination of the test, the fasteners were rinsed with water, blotted dry with a paper towel and inspected at low magnification (10X) for corrosion products.

RESULTS AND DISCUSSION

Hardness Test (MIL-STD-1312, Test No. 6)

Of the six types of experimentally coated fasteners tested, only one failed the Rockwell C38-45 hardness requirement of the basic fastener specification MS 16998. The diffused Ni-Cd, electroplated aluminum, IVD aluminum, chromium-zinc-flake coating, and the baked polymer-over-cadmium-plate coated fasteners all passed. All five of these fastener types had hardness values between Rc 42.1 and 42.8. The decomposition aluminum plated fastener type that failed, tested at an average of Rc 26.5. This reduction in hardness is probably due to the high temperature of the process. The two production lots of standard cadmium plated, chromated fasteners both passed with a Rockwell C hardness of 39.7 and 39.8.

Stress Durability (MIL-STD-1312, Test No. 5)

After exposing four fasteners from each lot and type to 200 hrs. of stress at 75% of their minimum ultimate tensile strength, they were removed and inspected from cracks. All of the fasteners passed the test. This indicated that the individual coating processes had not damaged or embrittled the fasteners.

Corrosion Resistance (MIL-STD-1312, Test No. 1)

After the coated fasteners had been exposed to the 5% salt spray test until failure had occurred or until the 45 day test period had elapsed, they were carefully examined. Test results are recorded graphically in Figure 1. Standard cadmium plated fasteners P/N MS16998-62 (0.2 mil & chromate coating) from stock were used as controls and failed after 15 days exposure (Figure 2).

IVD coated fasteners per MIL-C-83488 Class 3 (0.3 mil nominal) Type I (Not chromated) [ref (6)] failed after 4 days exposure (Figure 3). However, it should be noted that the IVD coating actually measured 0.2 mil [ref (7)]. The addition of a chromate coating deferred failure to 7 days; addition of a proprietary silicone coating delayed failure to 8 days; both the chromate plus the silicone coatings over the IVD coat postponed failure to 10 days.

IVD coated fasteners conforming to MIL-C-83488 Class 2, Type I (0.5 mil nominal) were removed from test after 18 days of exposure, because of the heavy aluminum corrosion products. However, base metal corrosion products were not evident (Figure 4). It should be noted that the coating thickness was actually 0.4 mil. When these fasteners were chromate coated (Class 2, Type II), they withstood 45 days of testing. Only one spot of base metal corrosion (red spot) products was evident (Figure 5).

Fasteners coated with 0.2 to .3 mils of electroplated aluminum failed after three day exposure (Figure 6). The addition of a chromate coating postponed failure to five days. The addition of a proprietary silicone coating over the chromated fasteners postponed failure to 10 days. Attempts to obtain thicker coatings were not sucessful. The vendor was no longer in the aluminum plating business.

Diffused nickel-cadmium plated fasteners failed after 15 days exposure with red corrosion products evident on most of the fasteners tested (Figure 7).

A proprietary baked polymer coating over electroplated cadmium did not fail after 45 days of exposure. The same coating over IVD aluminum coated fasteners conforming to MIL-C-83488 Class 3, Type II (chromated) also did not fail after 45 days exposure (Figure 8).

Chromium-zinc-flake coated fasteners resisted corrosion for twenty days before base metal corrosion products became visible. The addition of a proprietary silicone coating deferred failure to twenty seven days (Figure 9).

The decomposition plated aluminum coated fasteners failed after four days of test.

Environmental Tests

In the propulsion test stand exposure, the diffused nickel cadmium and the aluminum plated fasteners appeared to have coatings remaining on the exposed heads. The diffused nickel cadmium had changed in appearance from the dark brownish or bluish tint, to a silvery color, probably due to removal of the chromate treatment or dye. A spot test to determine if cadmium was still present was positive. The other coatings had disappeared leaving the bare fastener. After 24 hours in salt spray, the diffused nickel cadmium and the IVD aluminum were intact. The other fasteners rusted. Figure 10 shows the test block before exposure. Figure 11 shows the test block after exposure and salt spray. The breakaway torque after test was equal to or greater than the installation torque, indicating no damage to the fasteners.

All coatings withstood the one week immersion in fuel and seawater except the electroplated aluminum, which rusted in three days in the seawater layer. In the vapor test, the diffused nickel cadmium, the chromated and polymer coated IVD did not corrode. The standard cadmium plate discolored as did the polymer coated cadmium plate. The fasteners with the chromium zinc flake coating and the bare IVD had red rust showing.

Based on these tests, the diffused nickel cadmium and chromated IVD aluminum appear to withstand all of the environments of the underwater propulsion system. The 0.5 mil thickness of the IVD affords more protection than does the 0.3 mil coating. It was reported that the thinner coating was difficult to control, and would give inconsistent results. Also, the chromate conversion coating affords additonal protection to the IVD aluminum.

Electrochemical Tests

Initially, the corrosion potentials of the various coatings were cathodic to 7039, except for the chromium zinc flake coating which was slightly anodic. (Table II). The potential difference was highest with the diffused nickel-cadmium, approximately 400 millivolts, as compared to a 200 millivolt difference with the other coatings. The chromium zinc flake coating was 80 millivolts more negative, however, after four weeks, the potential of the coating had become more positive by 360 millivolts which made it cathodic to the 7039 aluminum.

The potential of the 7039 had shifted by 100 millivolts more positive during the test and the potential of the IVD shifted 70 millivolts more negative. Based on the potential difference of the diffused nickel cadmium and the chromium zinc flake coating, which were more cathodic than 7039, it was felt that they would not be compatible.

The galvanic current measurements show that the diffused nickel cadmium would not be compatible with 7039 aluminum. The current measured 150 $\mu a/cm^2$ for diffused nickel cadmium as compared to 5 $\mu a/cm^2$ for bare IVD and 0.25 $\mu a/cm^2$ for chromated IVD. This compares to 7.0 $\mu a/cm^2$ for the standard cadmium plating. While the weight loss was not determined, these measurements indicate that the corrosion rate of aluminum with diffused nickel cadmium would be considerably higher than with cadmium or aluminum coatings. With the chromated IVD the corrosion rate would be almost nil.

From these data, aluminum coatings appear to offer the desired corrosion protection for fasteners, if they are at least 0.4 mil thick. Initially 0.3 mil aluminum coatings, both IVD and electroplated, were requested since this is the present thickness of cadmium plating on fasteners and it was found that this thickness was not adequate. Gould's tests showed that 0.3 IVD aluminum coating on fasteners failed after 96 hours in salt spray. This compared to 768 hours reported for coated steel panels [ref (8)]. When questioned about this discrepancy the vendor had found that the process was difficult to control in the lower thickness range. Scanning Electron Micrographs (SEMS) of this group of fasteners showed the thickness was actually less than 0.2 mil. SEMS of fasteners with 0.5 mil coatings (nominal), showed the thickness to be approximately 0.4 mil. Specification MIL-C-83488 allows a tolerance of ± 0.1 mil on the 0.5 and 0.3 mil coatings. Therefore, the first group of coated fasteners did not meet the requirements of the specification while the second group did.

The second group of fasteners with the 0.5 mil coating showed much better corrosion resistance in salt spray and the environmental test, particularly with the vendor applied chromate conversion coating. However, this thickness could present problems in a class three fastener fit, which is a close tolerance fit.

The baked polymer coating also shows promise when applied over both cadmium and aluminum. This coating withstood the salt spray test with no failures and appears to be satisfactory in the fuel-salt water test. However, it will not withstand the engine exhaust environment. Also the additional thickness could present a problem on fit.

This program had only been concerned with finding coatings that would be a satisfactory replacement for cadmium from a corrosion standpoint.

A follow-on program will consider the following:

1. Installation torque values
2. The need for a thread lubricant and if so, which one.
3. Reusability, since the fasteners in the underwater system are resued many times.
4. Cost and availability
5. Performance in actual field use.

Conclusion

1. Ion vapor deposited aluminum per MIL-C-83488 Class 2 Type II appears to be a satisfactory replacement for cadmium plating.
2. Questions of fit, galling, and reusability would have to be studied before the coating could be recommended.

Acknowledgment

This work has been sponsored by Gould Inc. IR & D program under the sponsorship of the Ocean Systems Division.

References

1. E. Taylor, R. Burkhart, G. Gehring, "Corrosion Control of Fastening Systems for the Harsh Environments of Aircraft Carrier Steam Catapults" Paper No. 178 Corrosion/76.

2. F. Meyer, Jr., E. Jankowski, "Corrosion Performance of New Fastener Coatings on Operational Military Aircraft" Paper No. 115 Corrosion/73.

3. Military Standard 1312 "Fasteners, Test Methods."

4. R. Geisert, N. Greene, V. Agarwala "A Versatile Polarization Cell System" Corrosion, Vol. 32 No. 10 pp 407-410 (1976)

5. J. Von Fraunhofer, P. Staheli "The measurement of Galvanic Corrosion Currents in Dental Amalgams" Corrosion Science Vol. 12, p 767 (1972)

6. Specification MIL-C-83488 "Coating, Aluminum, Ion Vapor Deposited"

7. Private communication, McDonnell Aircraft.

8. Report IVD-080-07 "Ivadize - aluminum Plating by Ion Vapor Deposition" McDonnell Aircraft Co., Jan 14, 1977.

TABLE I

Coated Fastener Evaluation
Physical Test Results

SAMPLE	HARDNESS TEST (Rc 38-45)(1) Per MIL-STD-1312, Test No. 6	STRESS DURABILITY (200 Hrs)(2) Per MIL-STD-1312, Test No. 5
Diffused Nickel-cadmium (AMS 2416E, electroplated)	Rc 42.2	Pass
Electroplated Aluminum	Rc 42.1	Pass
Chromium-Zinc Flake (aqueous Dispersion, Bake)	Rc 42.2	Pass
Cadmium Plated + Baked Polymer	Rc 42.8	Pass
IVD Aluminum	Rc 42.3	Pass
Decomp. Plated Aluminum	Rc 26.5 (FAIL)	Pass
Control MS 16998-62	Rc 39.8	Pass

NOTES:

1) Requirement from the basic fastener specification MS 16998

2) Requirement from QQ-P-416, Cadmium Plating Specification

TABLE II
Coated Fasteners - Electrochemical Measurements

Coating	Corrosion Potential Volts vs Sat. Calomel Electrode Initial	4 weeks	Galvanic Current Coating vs 7039 Aluminum (ua/cm^2) Initial	24 hours
Diffused Nickel Cadmium	(-) 0.567	(-) 0.540	100	150
Electroplated aluminum	(-) 0.835	(-) 0.796	Not tested	
Chromium-Zinc-Flake	(-) 1.047	(-) 0.6871		
Cadmium Plate plus Baked Polymer Coating	(-) 0.765	(-) 0.788	Not tested	
IVD Aluminum 0.3 mil	(-) 0.795	(-) 0.864	Not tested	
0.5 mil (bare)			1.3	5.0
0.5 mil (chromated)	(-) 1.20	(-) $0.93^{(1)}$	3.8	0.25
Cadmium Plate Chromate Coating	(-) 0.784	(-) 0.792	60.0	7.0
7039 Aluminum Alloy	(-) 0.970	(-) 0.870		

Notes: 1) after 24 hours

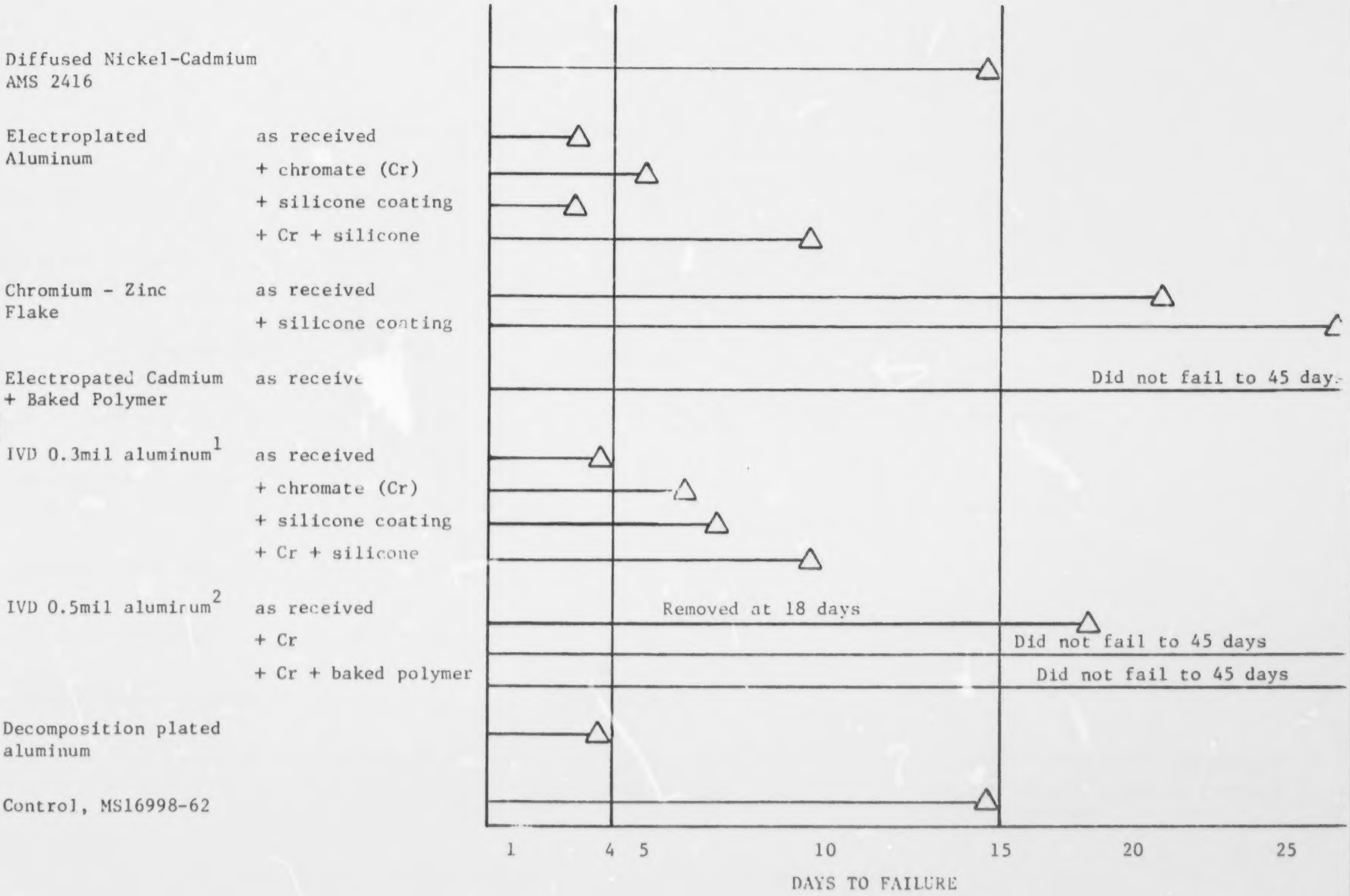


Figure 1. Salt Spray Test (5%)

NOTES: (1) Actual thickness less than 0.2 mil
(2) Actual thickness 0.4 mil

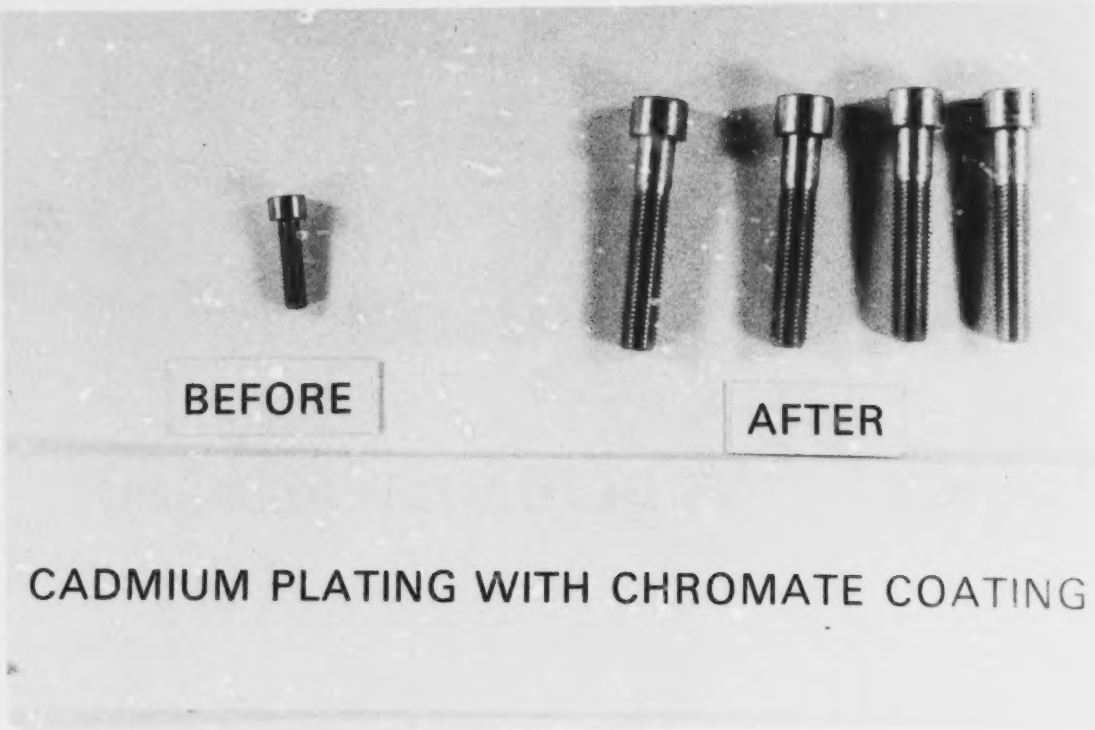


Figure 2 Salt Spray Exposure – 15 Days

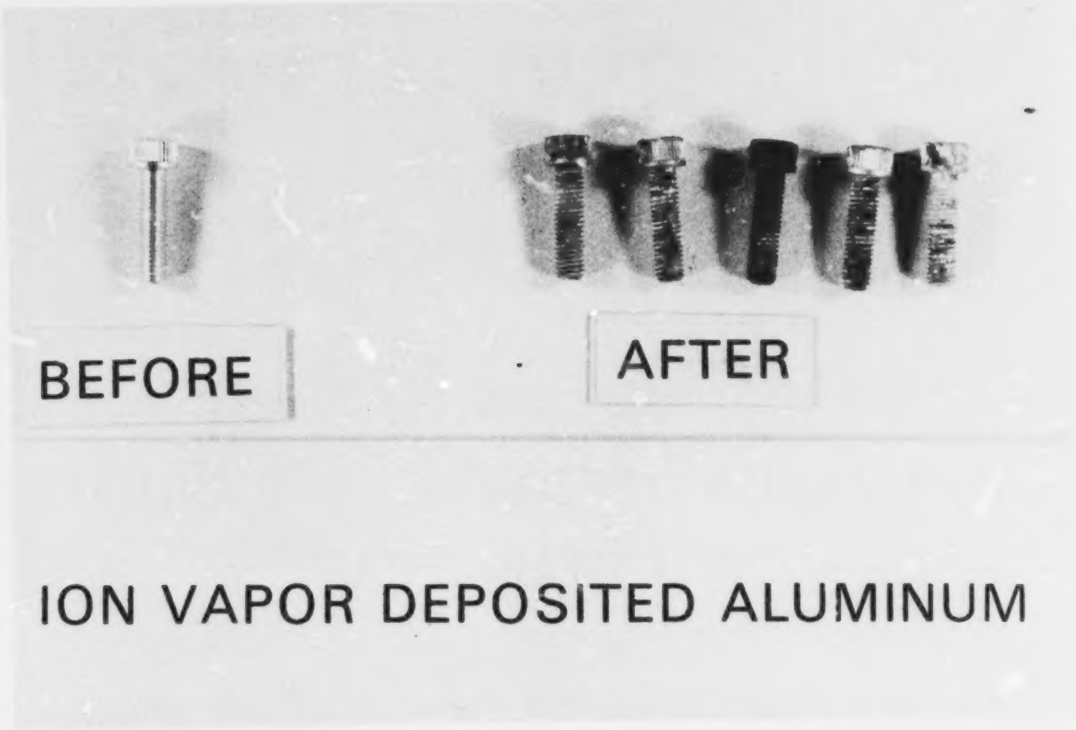


Figure 3 Salt Spray Exposure – 4 days

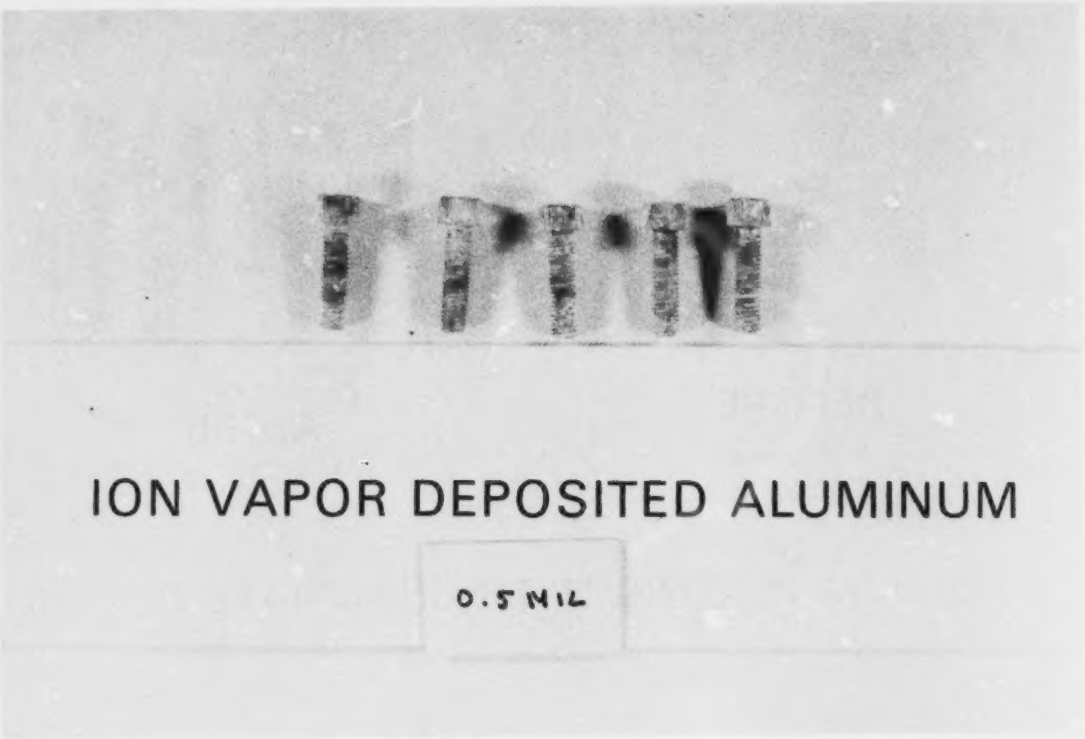


Figure 4 Salt Spray Exposure - 18 Days

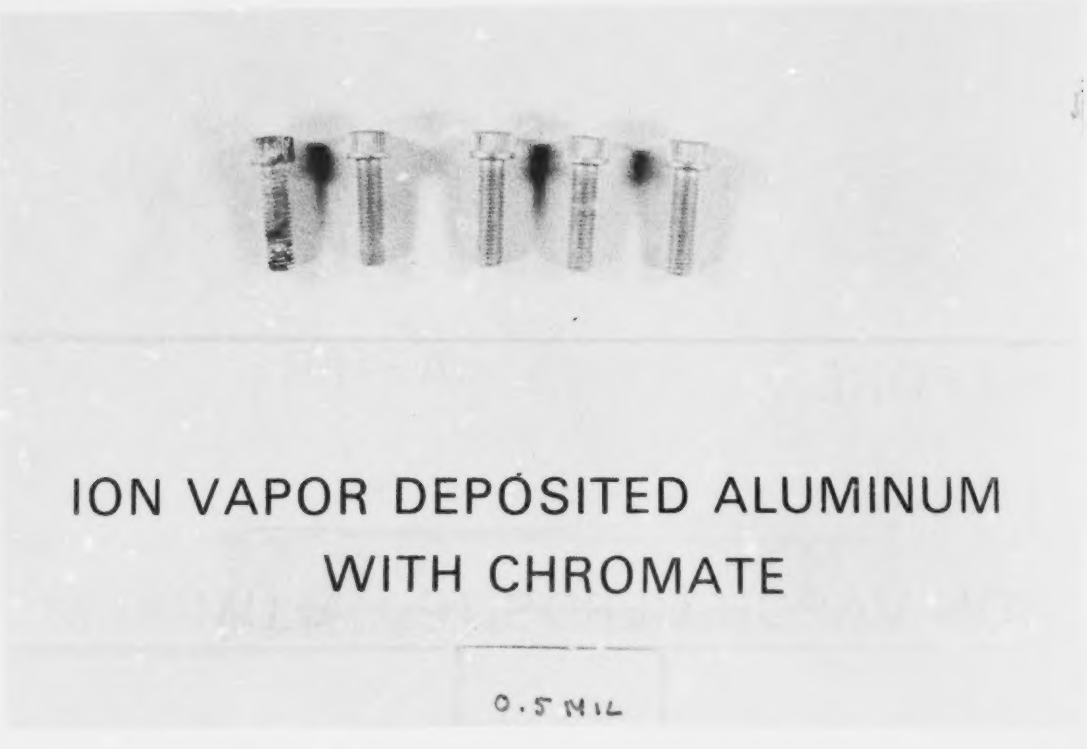


Figure 5 Salt Spray Exposure - 45 Days

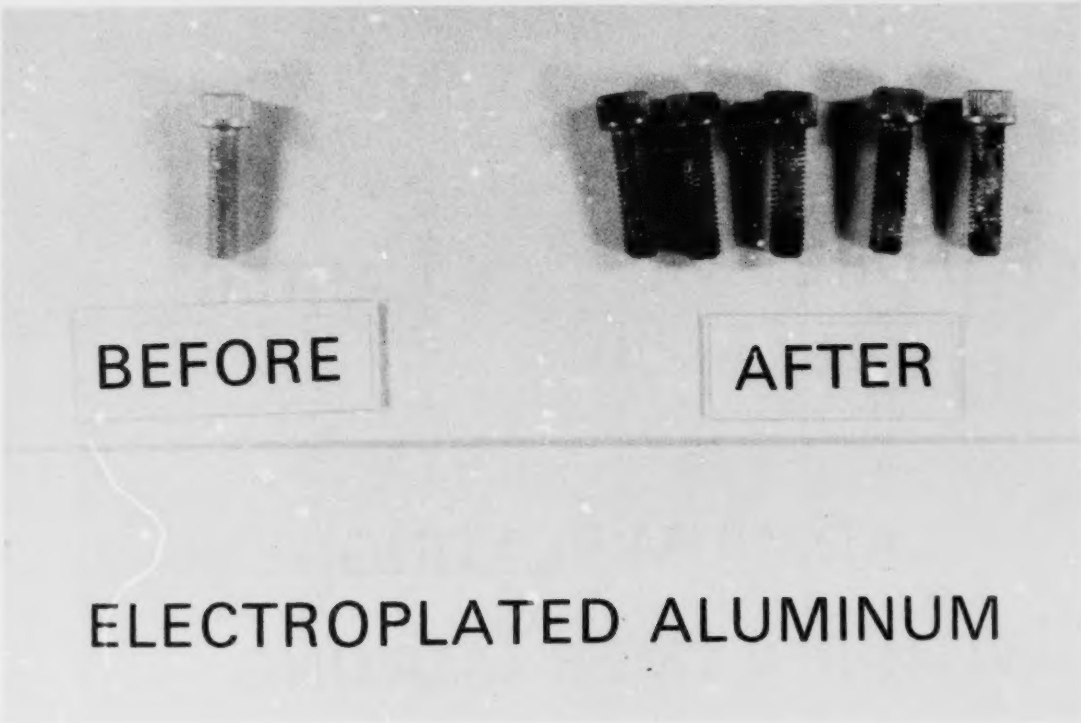


Figure 6 Salt Spray Exposure - 3 Days

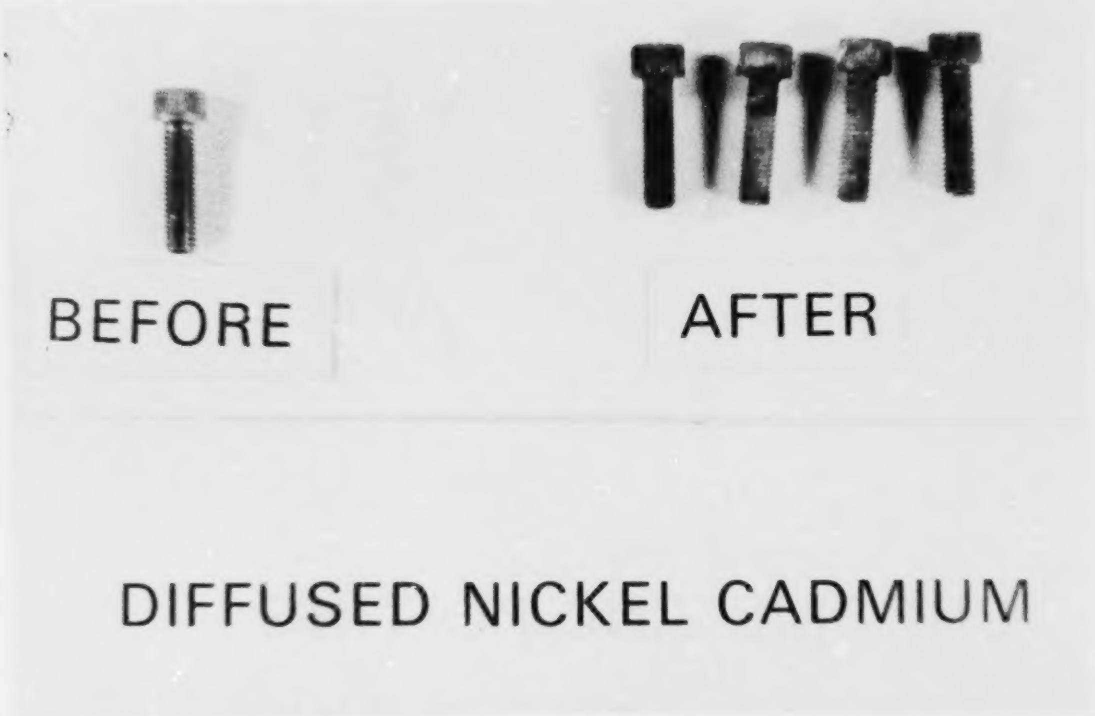


Figure 7 Salt Spray Exposure - 15 Days

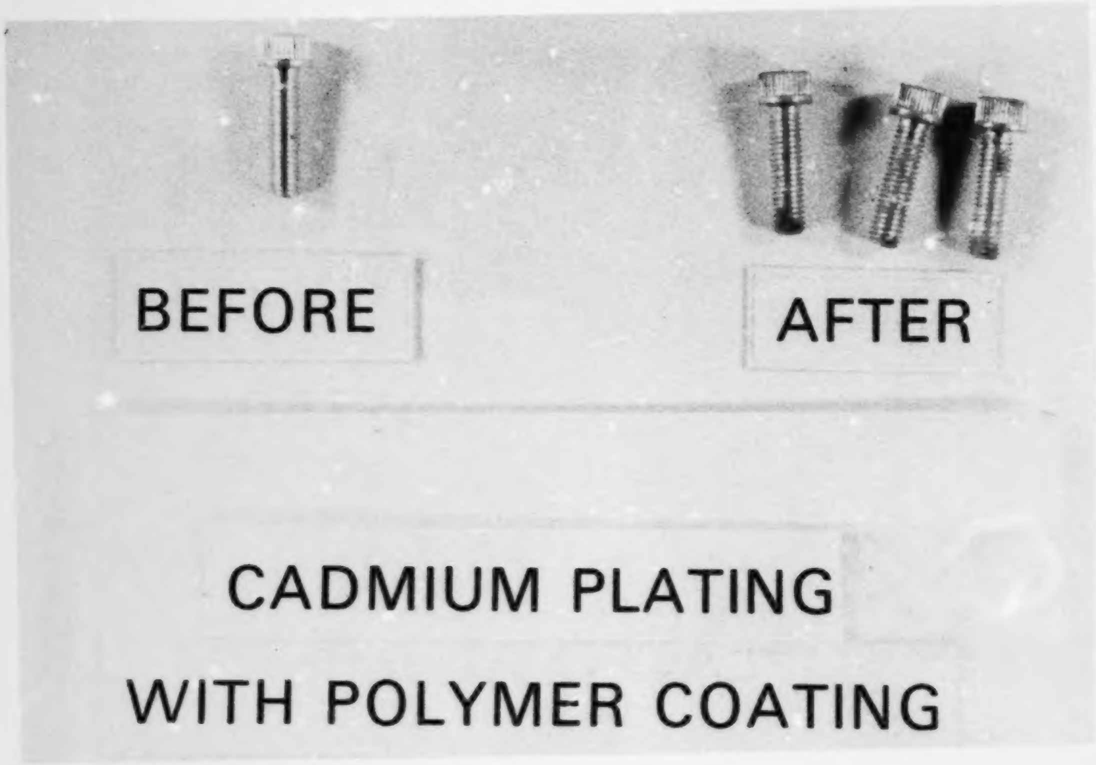


Figure 8 Salt Spray Exposure - 45 Days

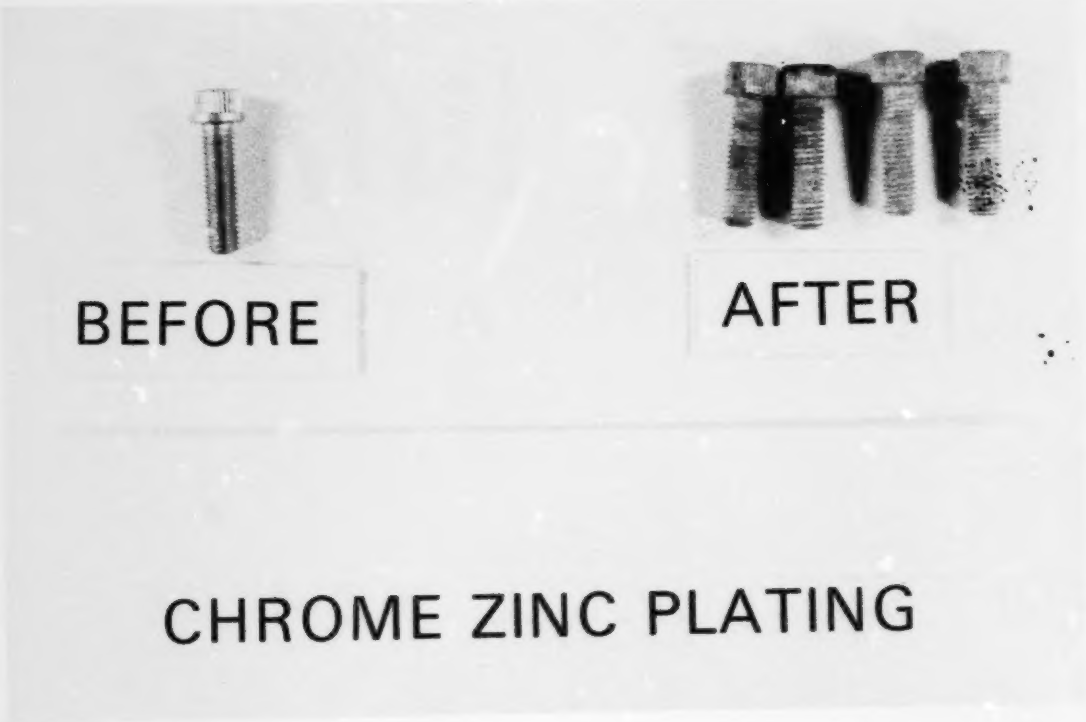


Figure 9 Salt Spray Exposure - 20 Days

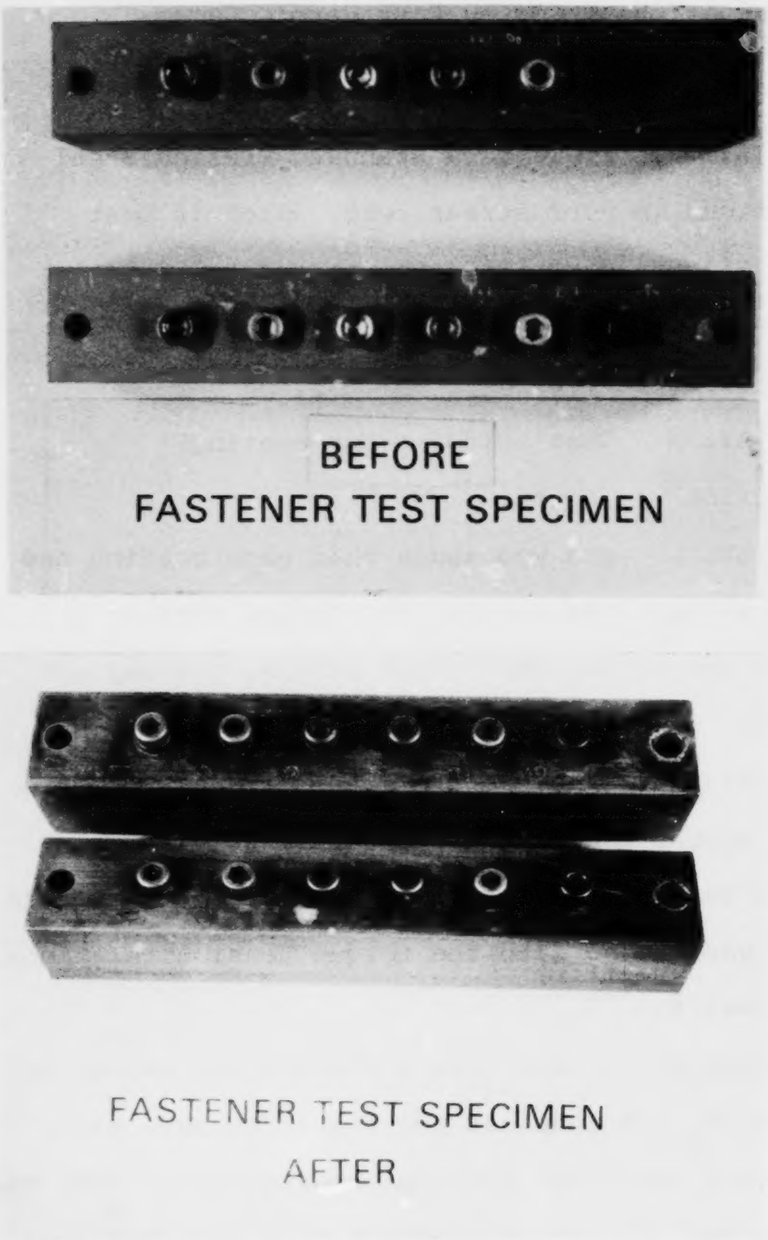


Figure 11

Fasteners Exposed to Combustion Products

Evaluation of Coated Fasteners: Alternatives to Cadmium Plating

Discussion Period

MR. TAYLOR: Ed Taylor, Standard Pressed Steel Company. I noticed in your stress test, which is Test Number five of Mil Standard 1312, you torque to 50 inch pounds.

MR. GEISERT: Yes.

MR. TAYLOR: That is for every coating?

MR. GEISERT: Right.

MR. TAYLOR: Are you aware that each coating and each different surface has a different torque tension behavior? When you torque the 50inch panels, you may not get the same load or the same tension in each case.

MR. GEISERT: Yes, we are aware of that and felt that using the graphite grease would equalize this. We recognized that there could be some difference, but at that time we didn't want to go into the torque tension relationship for each coating.

MR. TAYLOR: I have done a significant amount of work in this field. In the last two years, we have been looking for a more sensitive hydrogen embrittlement test and have found that Test Number Five of Mil Standard 1312 just does not satisfy our requirements.

We are currently employing a hydrotorque, which you are talking about, and we do not use the MilT5544, the graphite. We also have discovered that an angle block under the head seems to accelerate failure if hydrogen is present. We have also used another technique which automatically loads the screw to a predetermined load rather than depending on torque, and we find that this also works. You may want to be aware of these things for future testing.

The actual load that you imparted on the screws could have been less than 75 percent of the minimum alternate tensile strength because of the fact that the surface conditions are somewhat different. We have done the same thing and found that there is a lot of scatter. Hydrogen will be a lot easier to detect under higher loads.

You also mentioned that cadmium vaporizes at 450. Actually it melts at 612. The industry does not use it above 450 because of the threat of stress alloy cracking.

What I think is very important, and I will address this this afternoon, is the subject of post-plate embrittlement. This is embrittlement that occurs because of the anodic action of coatings or of structure with steel. In a marine environment, when you are coating or when your structure corrodes, you can develop hydrogen. This can diffuse into the steel, and you can get embrittlement. It doesn't matter what the coating is. I would suggest for further evaluation that you use a dead weight load test in a wet environment with your coatings. Surround them with a salt solution, hang them up with 75 percent of the minimum load on, minimum tensile strength, and see what happens. I think you will be amazed.

MR. MAYER: Jim Mayer, 3M Company. We have a little concern over the conclusions regarding your mechanical plating sample, and I guess we would like to express our willingness to make sure that in any confirmation studies which you do, you have coatings which are representative of what we feel we would like to be supplying.

MR. GEISERT: We went to local vendors who were using the 3M process. We did have good success with fasteners with larger thread diameter, larger threads, and we were told by them that because of the configuration of the threads, that the glass beads just could not get down into the roots.

Maybe you have improvements over that. This was a couple of years ago.

MR. MAYER: I would like Eddie Davis to answer that question.

MR. DAVIS: I think the proof is in the samples that everybody saw yesterday.

MR. GEISERT: I didn't see any 1032 screws there.

MR. DAVIS: We can certainly plate into small thread loops.

MR. GEISERT: I didn't see the size screws that we used.

MR. DAVIS: Whatever the size might be, we will plate into it. If you want to do any reevaluation as opposed to going to a vendor, submit the samples to us. We will be glad to plate them for you prior to your evaluation.

MR. GEISERT: Thank you.

MR. MAYER: I would like to add one other helpful remark to the previous questioner. There is a new hydrogen embrittlement study that is under ARP; I believe that is aircraft research procedure. It is a 200-hour pre-load test. That may or may not be helpful to you.

Evaluation of Alternatives

Session V

Thursday Morning 11:35

EVALUATION OF PROTECTIVE COATINGS FOR ARMY ORDNANCE ITEMS

Adolphe Edwards and William E. Isler
Harry Diamond Laboratories
Department of the Army
Adelphi, Maryland 20783

Corrosion protection alternatives to electro-deposited cadmium plating were evaluated by testing a number of defferent coatings on a currently produced artillery fuze sleeve. The presently used cadmium plating is covered by MIL-STD-171, Class 2, No. 1.1.2.2. with an exception that the inner surface coating may be 0.15 mils minimum. The dimensional tolerances of the sleeve allow a minimum clearance of 0.3 mils and the coatings evaluated conformed to these tolerances so that any acceptable alternative coating could be substituted without major design changes. The coatings tested include electroplated aluminum, electroplated zinc,electroless plated nickel, ion vapor deposited aluminum and an immersion coated zinc flake-chromium mixture. The coatings were tested for adhesion, porosity, salt spray corrosion resistance, thickness and thickness uniformity. Recommendations were made regarding the feasibility of using these alternative coatings based upon the test results.

Preceding page blank

EVALUATION OF PROTECTIVE COATINGS FOR ARMY ORDNANCE ITEMS

Adolphe J. Edwards and William E. Isler
Harry Diamond Laboratories, Adelphi, Maryland 20783

ABSTRACT

Corrosion protection alternatives to electrodeposited cadmium plating were evaluated by testing a number of different coatings on a currently produced sleeve for an Army artillery proximity fuze. The presently used cadmium plating is covered by MIL-STD-171, Finish No. 1.1.2.2, Class 2, with an exception that the inner surface coating may be 0.15 mil thick (minimum). All of the coatings evaluated in this study were judged in accordance with MIL-STD-171. The coatings tested were of electroplated zinc, electroless plated nickel, ion vapor deposited (IVD) aluminum, and an immersion coated zinc flake/chromate mixture. The coatings were tested for thickness, thickness variation, adhesion, porosity, and salt spray corrosion resistance. The cadmium and aluminum coatings met all of the necessary standards. The zinc flake/chromate mixture met many of the requirements and warrants further study along with the IVD aluminum as alternatives to cadmium for corrosion protection on fuze sleeves.

EVALUATION OF PROTECTIVE COATINGS FOR ARMY ORDNANCE ITEMS

INTRODUCTION

The possibility of restrictions [1] on the electroplating of cadmium and perhaps, as suggested in some countries, restrictions on the use of cadmium itself is of great concern to the U.S. Army. Many Army ordnance items utilize electroplated cadmium for corrosion protection. The implementation of the aforementioned restrictions could cause major supply and logistics problems to the Army and indeed to the entire Department of Defense.

The Harry Diamond Laboratories (HDL) initiated a study to evaluate some alternative coatings to determine possible substitutes for electroplated cadmium in case restrictions are imposed. A currently produced artillery fuze sleeve was selected as the test item for this study. The presently used cadmium plating is covered by MIL-STD-171, Finish No. 1.1.2.2, Class 2, with an exception that the internal surface coating may be 0.15 mil thick (minimum). Class 2 designates 0.3 mil thickness with a supplementary chromate treatment. The coatings tested in this study were electroplated zinc (Iridite* supplementary chromate treatment), electroless plated nickel, ion vapor deposited (IVD) aluminum (chromated), and an immersion coated zinc flake/chromate mixture known as Dacromet† 320. Initially, electroplated aluminum was to be included in the evaluation, but the specimens could not be prepared in time for this initial phase of the program. Electroplated cadmium specimens, with supplementary chromate treatment, were included in the tests as standards for comparison. The dimensional tolerances of the sleeve are such that the maximum plating thickness allowable is approximately 0.6 mil. The coatings included in this study were intended to conform to this tolerance so that direct substitutions could be made without dimensional or design changes.

---

*Trademark of Allied Research Products, Inc.

†Registered trademark of Diamond Shamrock Corporation.

TESTING

The coatings were tested for thickness, thickness variation, adhesion, porosity, and salt-spray corrosion resistance. Thickness measurement methods included magne-gage [2], electron backscatter [3], and optical microscopy [4]. Initially, magne-gage and electron backscatter readings were made on all of the sleeves. Subsequent optical measurements were used to obtain calibration curves from which these readings could be converted to thickness values. The calibration curves provide nondestructive thickness test methods for future specimens. The optical thickness measurements were made on the smooth exterior and interior surfaces and on the crowns and roots of the interior threads so that thickness variations could be determined.

The plating adhesion was tested according to Military Specification QQ-P-416C, Section 4.5.2. This Specification allows the alternatives of scraping or shearing through the plating or repeated bending of plated sections until rupture occurs. The second alternative was chosen.

Vertical sections cut from the sleeves were bent back and forth until rupture occurred. The edges of the rupture surfaces were then examined at 4X magnification for signs of separation between the plating and the base metal.

The ferroxyl test [5] for porosity was performed on the inner and outer surfaces of sleeves with each type of coating. The procedure was as follows:

1. Coat one side of rag bond paper with 5% NaCl-5% clear gelatin solution, and then dry the paper.

2. Wet the test paper with 5% NaCl solution and hold the paper firmly against a plated surface for 10 min.

3. Develop the test paper in 5% potassium ferricyanide solution.

The NaCl solution passes through discontinuities such as pores and reacts with the base metal to form ferrous chloride. The ferrous chloride reacts with the potassium ferricyanide to give a blue precipitate, which marks the locations of the discontinuities. No porosity test is specified for these sleeves, but this information should be indicative of the mechanical protection offered by the coatings. This factor is of extreme importance for nonsacrificial coatings.

Salt spray corrosion resistance was tested on 12 sleeves with each ty[illegible] of plating. All sleeves were tested simultaneously under the conditions [illegible]fied by ASTM B117 for 96 hr. These conditions are listed in Table I. The sleeves were then rinsed with running water (Fig. 1) and blown dry. The results of all of the testing were evaluated and compared with those for electroplated cadmium to determine possible substitutes for this application.

RESULTS

The thickness data for all sleeves are shown in Table II. For the electroplated cadmium, the external surface thickness ranged from 0.3 to 0.4 mil (Fig. 2). Comparing the averages for the internal (Fig. 3) and external surface, the variation is about 0.1 mil. The coating thickness on the roots and crowns of the inside threads were above the 0.15 mil specified minimum. The thickness of the electroplated zinc coatings varied from 0.3 to 0.7 mil. The thickness variation between external and internal surfaces was 0.4 mil. The plating thickness on the external surface exceeded the 0.6 mil maximum in some instances. The coating thickness on the internal threads approached the lower specified limit. The electroless plated nickel coatings varied in thickness from 0.3 to 0.4 mil. The thickness variation between external and internal surfaces was actually less than 0.1 mil, which is the least variation of any of the coatings. The plating thickness pretty much conformed to specifications on all surfaces. The external surface thickness of the IVD aluminum ranged from 0.5 to 0.8 mil (Fig. 4). Comparing average external and internal surface (Fig. 5) thickness values gives a thickness variation of 0.4 mil. The coating thickness on the roots of the inside threads is near the lower limit of the specifications. The external surface thickness fails to meet the 0.6 mil specified maximum in some instances. The zinc flake/chromate mixture coating on the external surface varied from 0.4 to 0.7 mil (Fig. 6). Comparing the averages for the smooth areas of the external and internal surfaces (Fig. 7) indicates a thickness variation of 0.1 mil. There were, however, buildups at the roots of the internal threads (Fig. 8) that far exceed the allowable maximum of 0.6 mil.

The results of the adhesion tests are shown in Figures 9 and 10. The zinc flake/chromate mixture coating should have been tested by the alternative shearing method since it is applied by immersion. Under the bending test, this coating flaked off completely due to the severe bending angles applied (Fig. 9). None of the other coatings showed evidence of flaking or peeling adjacent to the rupture surfaces. An example of an adhesion test specimen which did not flake or peel is shown in Figure 10.

The results of the porosity tests probably really indicate "effective" porosity since sacrificial coatings would tend to deter any attack on the base metal. Indications of porosity or other discontinuities are manifest as dark (blue) spots on the test papers. The results are pretty much comparable for electroplated cadmium (Fig. 11) and electroplated zinc (Fig. 12). The electroless plated nickel coatings apparently contain a gross degree of porosity, particularly on the internal surfaces (Fig. 13). The results for IVD aluminum (Fig. 14) indicate a bit more porosity than for the first two coatings particularly on the internal surfaces. The zinc flake/chromate mixture coating results (Fig. 15) were essentially comparable to those for electroplated cadmium and zinc.

For the salt spray test, the specification control drawing [6] for this sleeve states that "Passing the test will require that no samples show signs of corrosion on the outside surface of the base of the sleeve from the bottom of the sleeve up to the first external thread." The electroplated cadmium specimens clearly passed this test in that they were completely unmarked (Fig. 16) after the 96 hr salt spray exposure. The electroplated zinc (Fig. 17) and the electroless plated nickel (Fig. 18) just as clearly failed the test as evidenced by the buildup of corrosion products in the specified area. The IVD aluminum coatings met the salt spray requirements spelled out in the Specification Control Drawing (Fig. 19). There were, however, areas on the internal surface where corrosion had proceeded even to the extent of penetrating the coating. The performance of the zinc flake/chromate mixture coating was marginal in that superficial markings were evident in the critical area (Fig. 20). There was, however, no evidence of penetration of the coating on either the external or the internal surface.

CONCLUSIONS

Although the scope of this intial phase of the study was insufficient to qualify any of the alternative coatings, some definite conclusions were drawn.

1. The thickness of the electroless plated nickel met the specifications. Although this study failed to establish the fact, it is anticipated that zinc can be electrodeposited to the required thickness specifications.

2. Adhesion appears to be no real problem for any of the coatings, although the zinc flake/chromate mixture probably should be tested differently.

3. Porosity is noproblem with any except the electroless nickel coating, for which the problem may be insurmountable.

4. None of the coatings was as resistant to salt spray corrosion as electroplated cadmium with supplementary chromate treatment (Fig. 21). The performances of the electroplated zinc and electroless nickel were clearly unacceptable. The performance of the IVD aluminum was acceptable, and that of the zinc flake/chromate mixture was sufficiently close to the MIL-STD to warrant further consideration.

PLANS

The search for suitable alternatives to electroplated cadmium for corrosion protection of Army ordnance items include the following:

1. Further testing of IVD aluminum and zinc flake/chromate mixture specimens that are prepared to strict thickness and thickness variation standards.

2. Testing of electroplated zinc coatings that have a more substantial, supplementary chromate treatment.

3. Testing of electroplated aluminum coatings with supplementary chromate treatment.

4. Testing of other organic, inorganic, and plastic coatings.

ACKNOWLEDGEMENTS

We appreciate the encouragement and support of H. Suminski of HDL. We also thank J. A. de Riddler and J. R. Kovelan of Diamond Shamrock Corporation and E. R. Fannin and J. J. Reilly of McDonnell Aircraft Co. for supplying some of the coated specimens.

TABLE I

ASTM B117

PARAMETER	DATA
SUSPENSION	15 TO 30 DEG FROM VERTICAL
SALT SOLUTION	5 ± 1:95 $NaCl:H_2O$
pH RANGE (ATOMIZED AT 30°C)	6.5 TO 7.2
COMPRESSED AIR SUPPLY	10 TO 25 PSI
TEMP. OF EXPOSURE ZONE OF CHAMBER	35 + 1.1 - 1.7°C

TABLE II

COATING THICKNESS (MIL)					
MATERIAL	EXTERNAL SURFACE	INTERNAL SURFACE	VARIATION	INTERNAL THREAD ROOT	INTERNAL THREAD CROWN
ELECTRO-PLATED CADMIUM	0.4	0.3	0.1	0.2+	0.3
ELECTRO-PLATED ZINC	0.7	0.3	0.4		
ELECTROLESS PLATED NICKEL	0.3	0.2	0.1	0.2+	0.4
ION VAPOR DEPOSITED ALUMINUM	0.7	0.3	0.4	0.2-	0.3
ZINC FLAKE/ CHROMATE MIXTURE	0.4	0.5	0.1	5.0	0.2

REFERENCES CITED

1. Code of Federal Regulations: Title 40 - Protection of Environment, Part 413.

2. Brenner, A. J., Res. Nat'l Bur. Stds., 18, 565 (1937).

3. Clarke, E., et. al., Elec. Eng., 70, 35 (1951).

4. Burns, R. M., and Bradley, W. W., Protective Coatings for Metals, Reinhold, (1967), p. 330.

5. Burns, R. M., and Bradley, W. W., ibid., p. 336.

6. HDL Specification Control Drawing #19202.

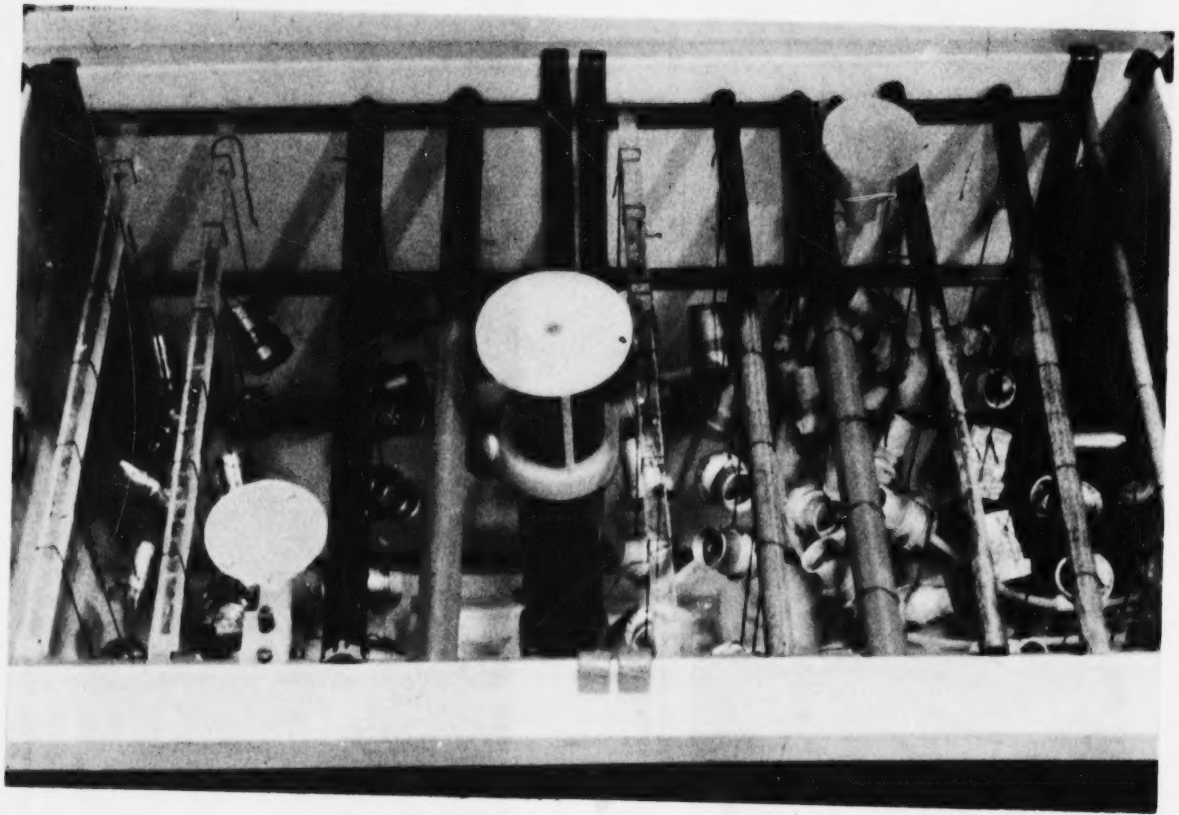


Fig. 1 Salt spray chamber with test specimens in place

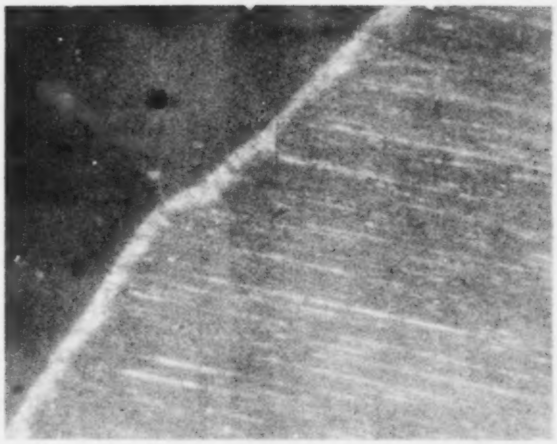


Fig. 2 Section showing Cd plating thickness on external surface 250X

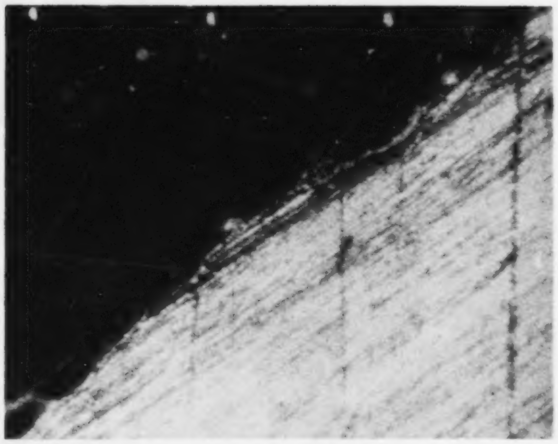


Fig. 3 Section showing Cd plating thickness on internal surface 250X

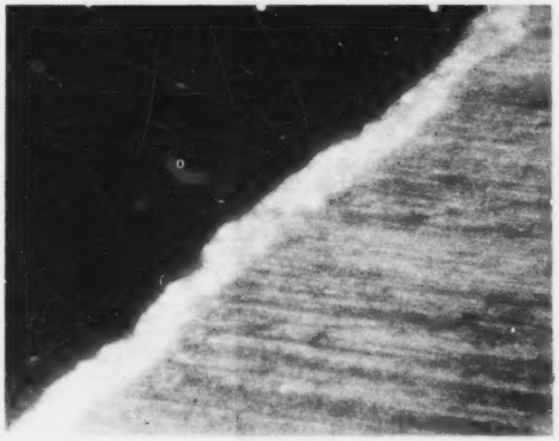


Fig. 4 Section showing IVD Al coating thickness on external surface 250X

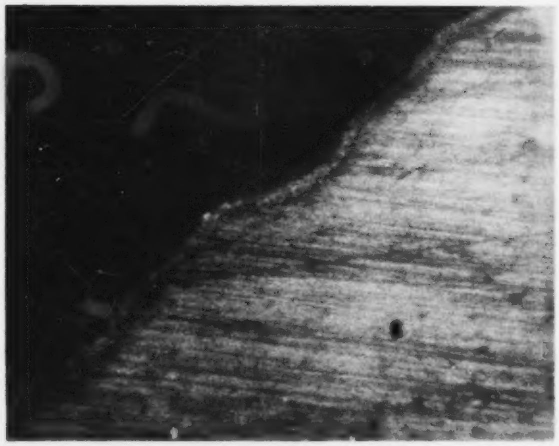


Fig. 5 Section showing IVD Al coating thickness on internal surface 250X

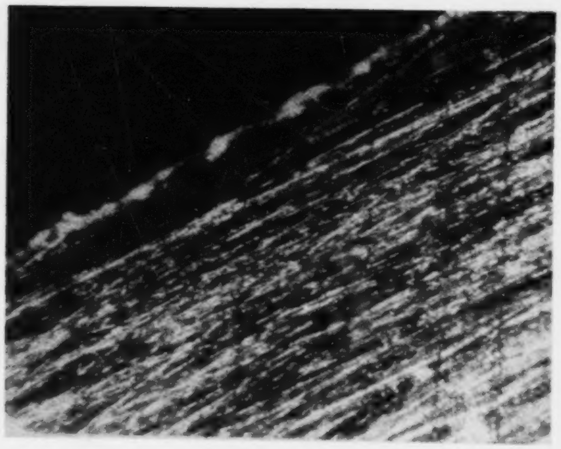


Fig. 6 Section showing zinc flake/chromate coating thickness on external surface 250X

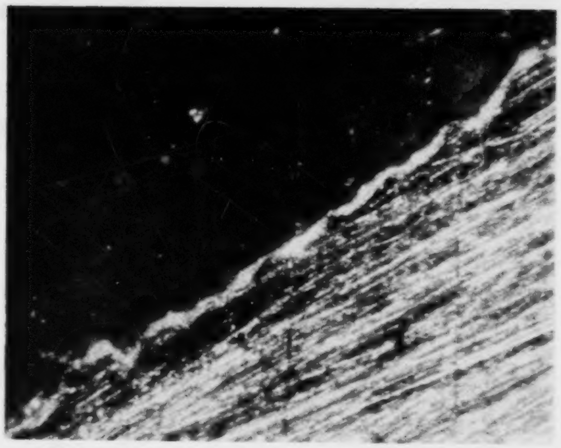


Fig. 7 Section showing zinc flake/chromate coating thickness on internal surface 250X

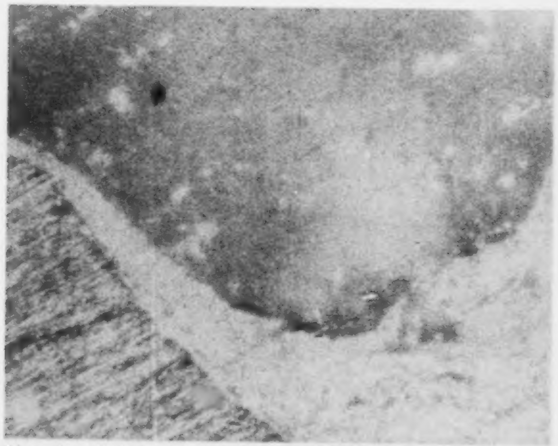


Fig. 8 Buildup of zinc flake/chromate coating in roots of internal threads 250X

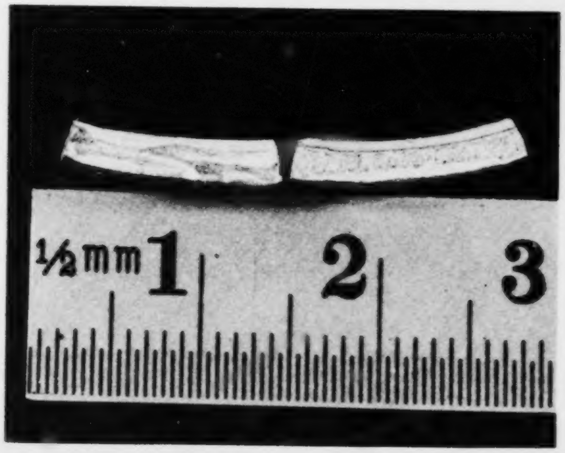


Fig. 9 Zinc flake/chromate mixture coated adhesion test specimens

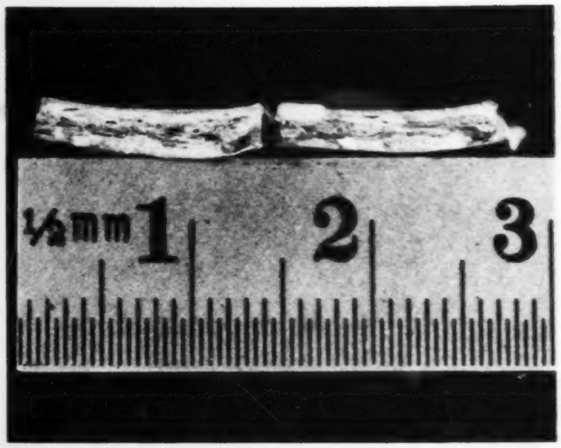


Fig. 10 IVD aluminum coated adhesion test specimens.

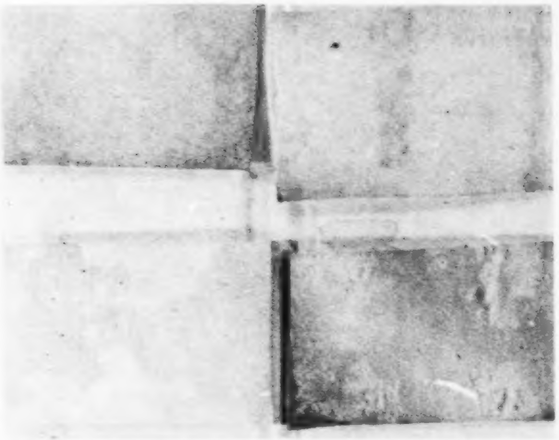


Fig. 11 Results of porosity test on electroplated cadmium External surfaces at top--internal surfaces at bottom

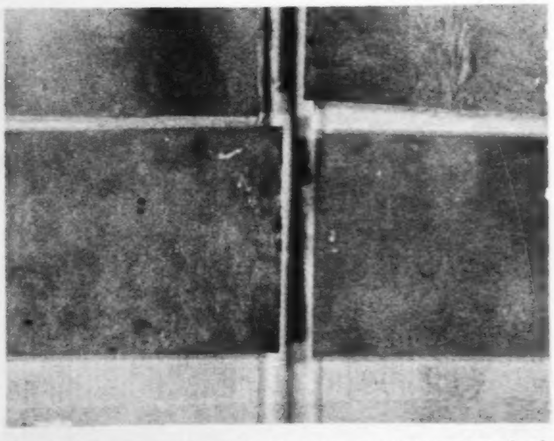


Fig. 12 Results of porosity test on electroplated zinc coating External surfaces at top--internal surfaces at bottom

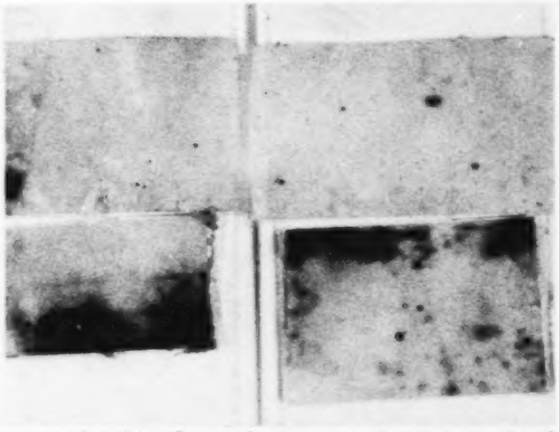


Fig. 13 Results of porosity test on electroless plated nickel coating External surfaces at top--internal surfaces at bottom.

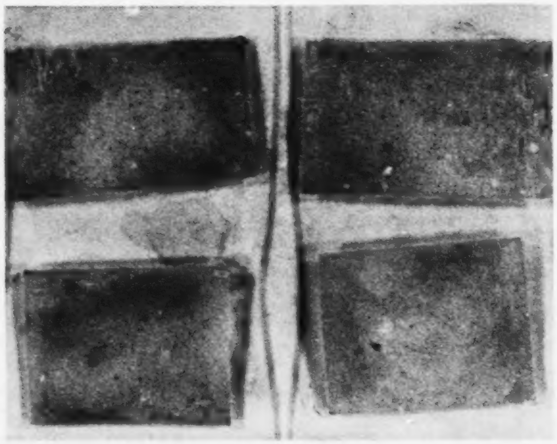


Fig. 14 Results of pososity test on IVD aluminum coating External surfaces at top--internal surfaces at bottom

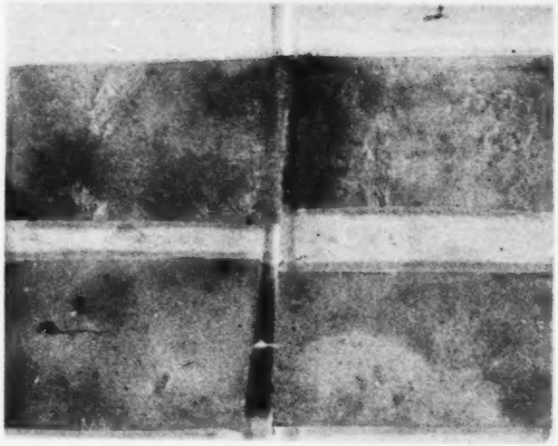


Fig. 15 Results of porosity test on zinc flake/chromate coatings External surfaces at top--internal surfaces at bottom

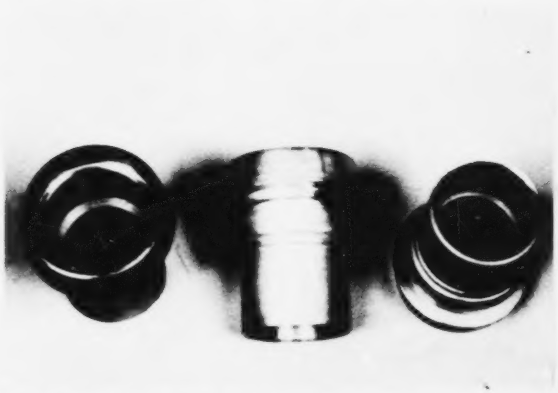


Fig. 16 Electroplated cadmium salt spray test specimens

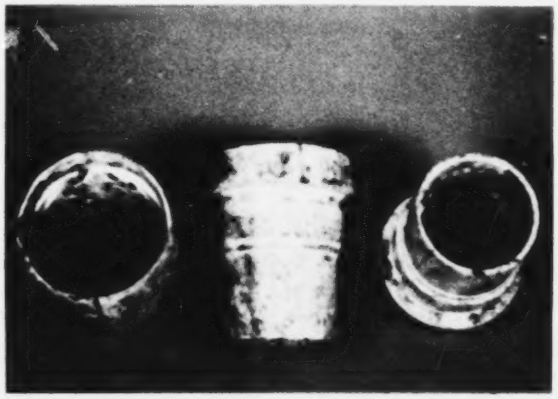


Fig. 17 Electroplated zinc salt spray test specimens

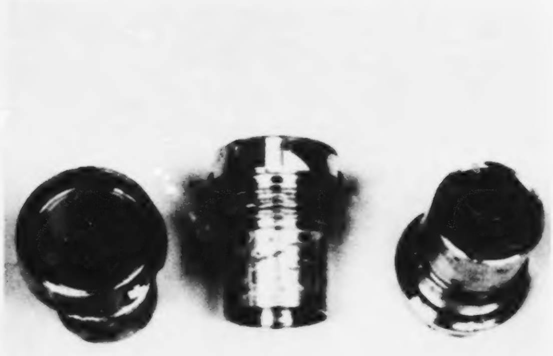


Fig. 18 Electroless plated nickel salt spray test

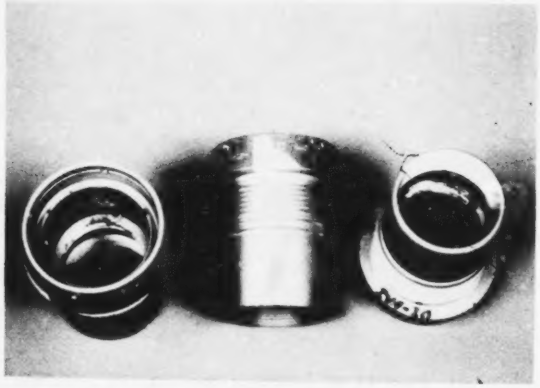


Fig. 19 IVD aluminum coated salt spray test specimens

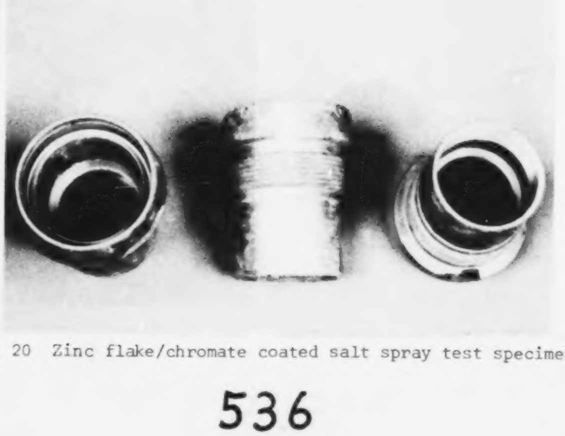


Fig. 20 Zinc flake/chromate coated salt spray test specimens

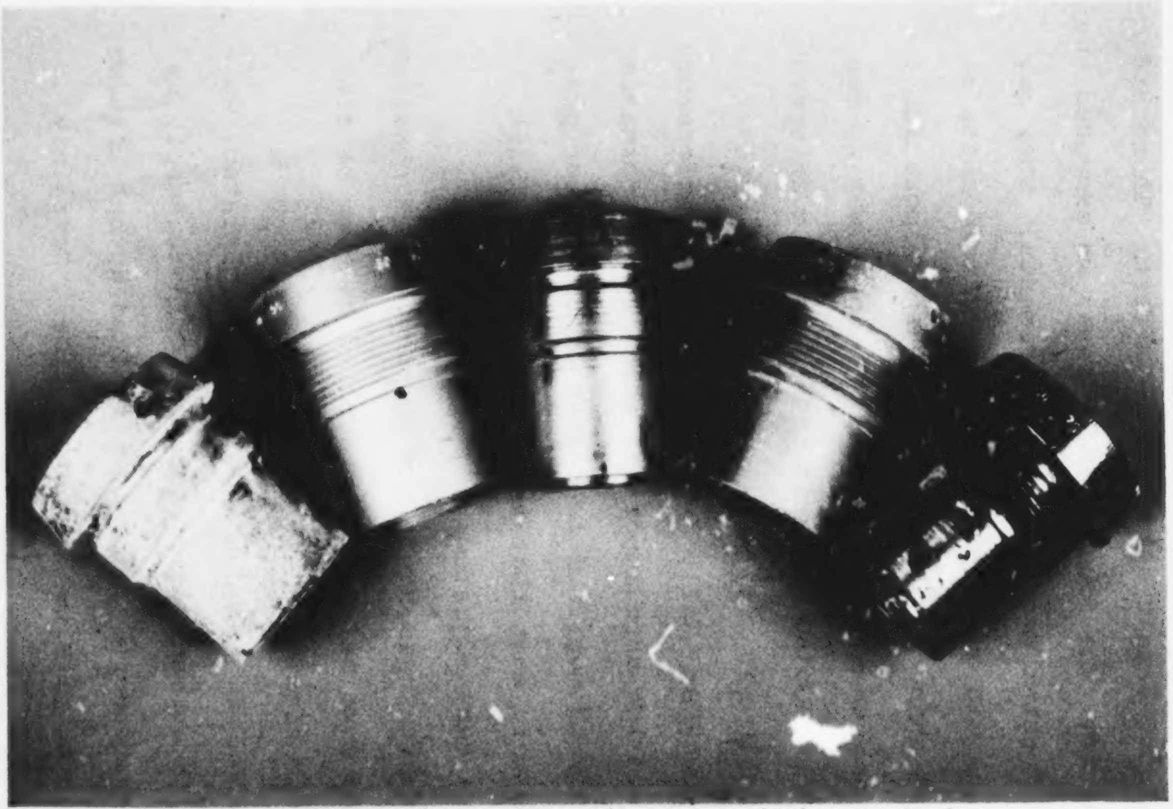


Fig. 21 Salt spray test specimens of (from left to right) electroplated zinc, IVD aluminum, electroplated cadmium, zinc flake/chromate mixture, and electroless plated nickel coatings

Evaluation of Protective Coatings for Army Ordinance Items

Discussion Period

MR. KOVELAN: John Kovelan, Diamond Shamrock. Thank you very much for your study. One of the things I mentioned during my talk was that there are a lot of people that don't accept the salt spray box as a test. There are diversities in them. We found in most cases we exceeded the standards, and I think we met your requirements. They may have been marginal in a few places, but our field tests at Curry Beach, and those performed by Dualvast Corporation over a twoyear period were excellent. The only way we can look at these tests objectively is to use them in an operational, functional way.

MR. EDWARDS: Well, I agree that high performance in the field is a lot more important than high performance in the salt spray chamber. I feel that probably your process parameters were such that they could pass the salt spray test, were they adjusted.

MR. MAYER: Jim Mayer, 3M Company. What consideration did you give to mechanically applied cadmium or zinc coatings for your testings?

MR. EDWARDS: When this study was initiated, we made contact with as many vendors as we could to supply us with coatings, but there were only a limited number that we contacted due to the limited amount of time. Certainly future plans would include such coatings.

MR. MAYER: We would like to have you look at both of those, and perhaps consider the use of our sulfate cadmium plating bath as a comparison to the cyanide with which you are working.

MR. EDWARDS: We would be happy to do so.

MR. ZEHNDER: Joe Zehnder, Enthone Incorporated. I was very surprised to see the results you found with electroplated zinc because people are plating zinc and are getting 96 hour salt spray resistance every day. I would like to comment on the unrealiability of the salt spray tests.

Committee B-8 of ASTM is actively investigating the variations that are observed from cabinet to cabinet. If there is anybody here that would like to get involved in this evaluation, they should contact Mr. Cobb at ASTM. I am sure that he could make arrangements for them to participate in this.

There has been some data received from Australia recently where they had five test boxes that they ran these same specimens through and they got five different answers.

MR. EDWARDS: That is entirely possible. That was the reason for our including the cadmium standards in the same chamber at the same time. All the specimens were in the chamber at the same time and were exposed to the same conditions, and I think it is meaningful that cadmium did not have a mark on it and some of the other coatings were pretty well deteriorated.

MR. ZEHNDER: I agree with you, but there are different chromate coatings for zinc than there are for cadmium.

MR. EDWARDS: We do plan to look at zinc with a more substantial chromate coating.

Evaluation of Alternatives

Session V

Thursday Morning 12:10

CORROSION PERFORMANCE OF NEW FASTENER COATINGS ON OPERATIONAL MILITARY AIRCRAFT

Edward Jankowsky
Fred H. Meyer, Jr.
Air Force Materials Laboratory
Department of the Air Force
Wright-Patterson Air Force Base, Ohio 45433

Cadmium plating as currently used for the sacrifical corrosion protection of steel fasteners used in aircraft has a relatively short service life on operational equipment. Many potential replacement coatings with greater durability have been proposed throughout industry but very little actual service experience has been available to properly evaluate the coatings.

The commonly accepted practice of applying 0.2 mil of cadmium plate per QQ-P-416, Type II, Class 3, as fastener protection has been totally inadequate for aeronautical use and a concerted effort by the Aerospace Industries Association and others concerned has effected a change to 0.3 mil of cadmium (QQ-P-416, Type II Class 2). This thickness still is not totally satisfactory.

The Air Force Materials Laboratory initiated a program in 1964 to evaluate high purity aluminum coatings on standard aircraft fasteners utilizing an HC-130H Aircraft.

This pioneering study showed that aluminum coatings performed as well as a cathodic protection coating for steel fasteners with the added advantage of compatibility with the primary aluminum airframe materials. It was shown that the aluminum coatings should be a least .0005 inch thick for extended service life, however. This places an additional burden in determining the feasibility of replacing cadmium coatings with aluminum coatings. Since the period of this earlier study a number of more economical aluminum coating processes have been developed.

The program which is the subject of this paper was initiated in 1969 as an expansion of the earlier program. Many candidate coatings were offered by a wide cross section of the aerospace industry for screening in this program. This program is but a first step in the final selection of new fastener coatings for general usage since side effects such as torque-tension relationship must be evaluated along with joint fatigue strengths.

CORROSION PERFORMANCE OF NEW FASTENER COATINGS ON OPERATIONAL MILITARY AIRCRAFT

Fred H. Meyer, Jr.

Air Force Materials Laboratory, Wright-Patterson AFB, Ohio

Edward J. Jankowsky

Naval Air Development Center, Warminster, Pennsylvania

INTRODUCTION:

Cadmium plating as currently used for the sacrificial corrosion protection of steel fasteners used in aircraft has a relatively short service life on operational equipment. Many potential replacement coatings with greater durability have been proposed throughout industry but very little actual service experience has been available to properly evaluate the coatings.

The commonly accepted practice of applying 0.2 mil of cadmium plate per QQ-P-416, Type II, Class 3, as fastener protection has been totally inadequate for aeronautical use and a concerted effort by AIA and others concerned have effected a change to 0.3 mil of cadmium (QQ-P-416, Type II, Class 2). This thickness still is not totally satisfactory.

The Air Force Materials Laboratory initiated a program in 1964 to evaluate high purity aluminum coatings on standard aircraft fasteners utilizing an HC-130H Aircraft. Results of this study are available in Reference 1 and 2.

This pioneering study showed that aluminum coatings performed well as a cathodic protection coating for steel fasteners with the added advantage of compatibility with the primary aluminum airframe materials. It was shown that the aluminum coatings should be at least .0005 inch thick for extended service life, however. This places an additional burden in determining the feasibility of replacing cadmium coatings with aluminum coatings. Since the period of this earlier study a number of economical aluminum coating processes have been developed.

The program which is the subject of this paper was initiated in 1969 as an expansion of the earlier program. Many candidate coatings were offered by a wide cross section of the aerospace industry for screening in this program. This program is but a first step in the final selection of new fastener coatings for general usage since side effects such as torque-tension relationship must be evaluated along with joint fatigue strengths.

Four operational C-141 Aircraft were utilized as flying laboratories by the Air Force for the exposure candidate materials supplied by a wide cross section of industrial corporations. A-7 and RA-5 Aircraft were utilized by the Navy. The use of aircraft was deemed necessary since accelerated screening tests have been proven to be unreliable as a basis for the prediction of performance of coatings in service. Since the operational environment profiles of Naval and Air Force aircraft are somewhat different, a number of the same coatings were also tested on A-7 and RA-5 Aircraft under the direction of the Naval Air Development Center.

TESTING PROCEDURES

To reduce the variability of basis metal quality all fasteners in the Air Force program were supplied in the uncoated condition to all participants by one supplier. The Navy chose to strip fasteners from field inventory for replating by the participants.

Three specific panel locations were chosen on each Air Force test aircraft type to allow a spectrum of environmental exposure to affect the fasteners, i.e. one panel was chosen on top of the aircraft, one on the side and one on the bottom. The standard fasteners were removed on the panels chosen for test and replaced with triplicate specimens of each type of fastener candidate. NAS 1203 standard fasteners were used for the C-141 program. All participants were asked to supply their fasteners with a nominal .3 - .4 mil coating. Some of the candidate materials were supplied in greater thicknesses. However, these were tested as received. The suitability of the coating will be based on the supplied thickness. This will impose an additional economic competitive burden on those suppliers who for one reason or another were unable to meet the 0.3 - 0.4 mil criteria. Costing thicknesses of supplied fasteners were checked using microscopic sectioning per ASTM B 487-72.

Arrangements were made with Military Airlift Command personnel at McGuire AFB to inspect the C-141 aircraft fasteners at six month intervals or less, for corrosion. Assistance was also provided by the Naval Air Development Center and by the SPS Company in evaluating fastener corrosion. Final testing and removal was planned for a two years total exposure. A complete itinerary of each C-141 by theater of operation was maintained by the MAC office for use in determining the environmental profile of each of the test installation.

Navy fasteners were also inspected at six month intervals. Navy tests were for a total exposure time of one year-six months on a carrier and six months of land based operations with short trips to a carrier and back.

The holes were examined for any observable corrosion at the time of the fastener removals. Identical fasteners of most of the candidate materials were also exposed on ground environmental test racks at McGuire AFB, New Jersey and McChord AFB, Washington. Coatings were considered disqualified for further testing when all the coating had been expended on the head of the fastener and were then removed from the aircraft or rack.

RESULTS

An analysis of the test results obtained showed a marked greater level of corrosion severity on nearly all coatings on the top of the aircraft where the fastener heads were directly exposed to weather conditions. On the side and bottom of the aircraft many coatings survived which failed on the top of the aircraft. Very little evidence of damage was observed on the airframe countersink areas around the fasteners. For purposes of choice for further testing the survivability of the coating on the top of the aircraft for the two year test period has been chosen as the acceptability criteria.

Results of test by the Air Force and the Navy are in good agreement in spite of differences in environmental conditions. Slight differences that exist may be accounted for by the shorter Navy exposre time.

CONCLUSIONS

Those candidates based on aluminum coatings deposited by either an electro-deposition from an ether based process or ion vapor deposition show a marked superiority over "standard" cadmium plate in survivability. Also one type of a proprietary metallic ceramic also survived. Minimum coating thicknesses of 0.4 mils appear to be desirable for consistent performance. From the production process standpoint the ion vapor deposition process is currently the most practical technique. Reference to the presentation by McDonnell Douglas on Tuesday is advised. A MIL-SPEC-MIL-C-83488(USAF) covers this process.

REFERENCES

1. W. C. Herron, Service Evaluation of Aircraft Experimental Fasteners, AFML TR-67-360, November 1967.

2. W. A. Boggs, W. C. Herron, Evaluation of Fasteners and Corrosion Prevention Techniques on HC 130H S/N 64-14861, Lockheed Georgia Co. ER 9587-5, 31 December 1969.

3. E. J. Jankowsky, Fastener Coating Service Evaluation Progress Report, Naval Air Development Center NADC-MA-7151, 11 February 1972.

PERFORMANCE OF COATINGS ON C-141 AIRCRAFT

2 YEAR EXPOSURE

TYPE	THICKNESS/MILS	MONTHS AVERAGE TO FAILURE
CADMIUM PLATE	0.3	10
CADMIUM PLATE + INHIBITIVE SEALANT	1.0	15
ALUMINUM PLATE (FUSED SALT)	0.4	10
ALUMINUM PLATE (ETHER BATH)	0.7	24 +
ALUMINUM PLATE	0.6	24 +
DUAL EPOXY	0.8	21
IVD ALUMINUM	0.5	24 +
TI-CD + CONV COATING	0.4	10
ALUMINUM PLATE (FUSED SALT)	0.3	24 +
ALUMINUM PLATE IMMERSION	0.5	21

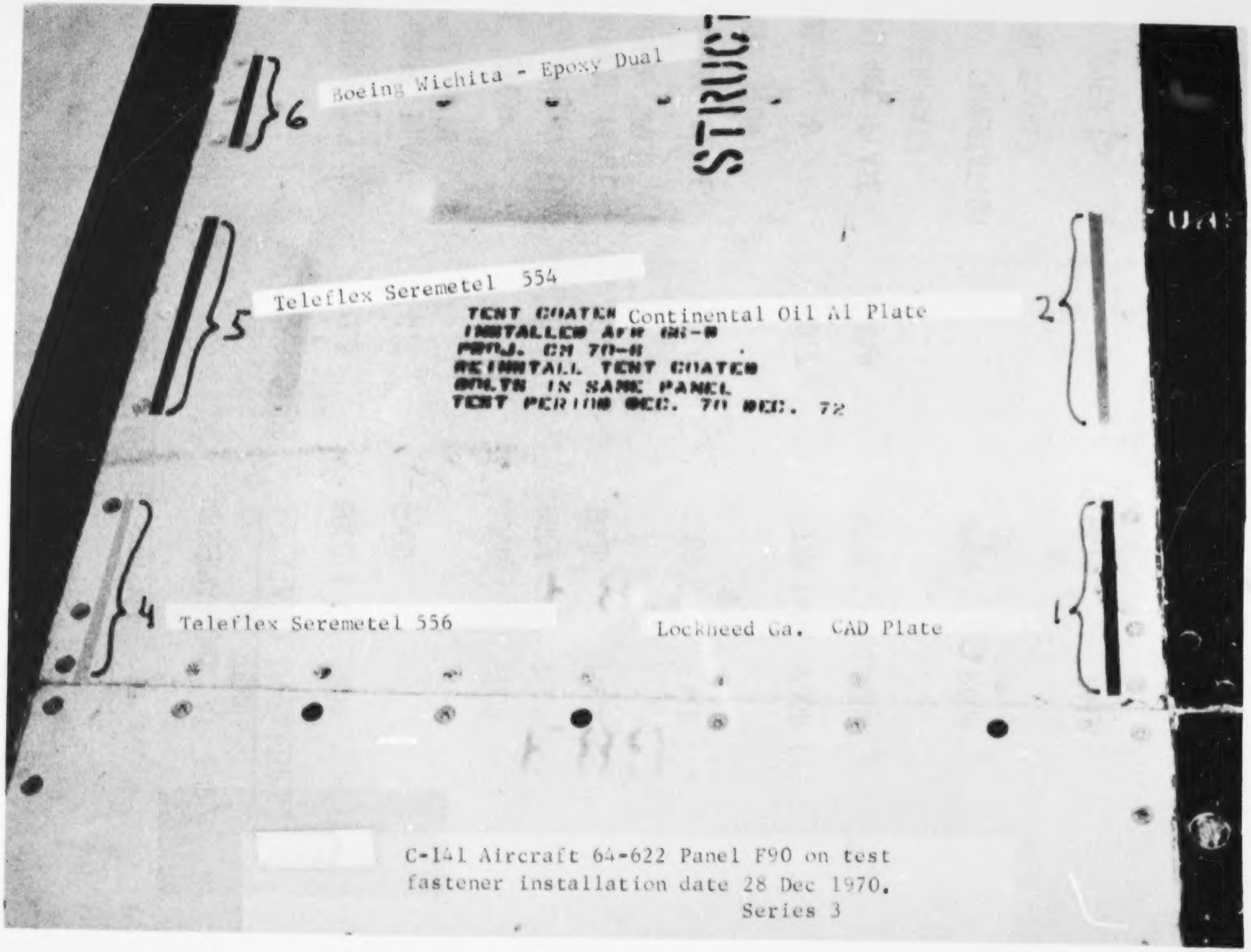
PERFORMANCE OF COATINGS ON
C-141 AIRCRAFT
2 YEAR EXPOSURE

TYPE	THICKNESS/MILS	MONTHS AVERAGE TO FAILURE
SERMETEL 556	0.3	12
SERMETEL 554	0.8	21
SERMETEL 555	0.7	14
SERMETEL W	0.7	14
ALUMINUM PLATE (ETHER BATH)	0.4	11
SWAGED ALUMINUM WASHER	-	10
CAD-TIN-MECH PLATE	0.4	10
CAD-MECH PLATE	0.4	10
ARMCO PROPR INORGANIC COATINGS (I-V)	-	13

PERFORMANCE OF COATING ON A-7 AND RA-5 AIRCRAFT

1 YEAR EXPOSURE - CARRIER SERVICE

TYPE	THICKNESS/MILS	OBSERVATIONS AT END OF TEST	
		A-7 (TAIL)	RA-5 (TOP)
CADMIUM PLATE	0.3	GOOD (-)	POOR
ALUMINUM PLATE ETHER BATH	0.7	GOOD	
DUAL EPOXY		GOOD (-)	POOR
TI-CD + CONV COAT	0.4	POOR (+)	POOR (+)
ALUMINUM PLATE FUSED SALT	0.3	GOOD	FAIR (-)
ALUMINUM PLATE IMMERSION	0.5	GOOD	FAIR (-)
SERMETAL W	0.7	POOR (+)	POOR (+)
ALUMINUM PLATE ETHER BATH	0.4	GOOD	GOOD
PACK CEMENTATION (SI MG-AL)	-	POOR	POOR
TIN OVER CD	-	FAIR	FAIR



C-141 Aircraft 64-622 Panel F90 on test fastener installation date 28 Dec 1970.
Series 3

[redacted]. C-141 Aircraft 64-638 used as [redacted] test bed.

549

Corrosion Performance of New Fastener Coatings on Operational Military Aircraft

Discussion Period

MR. SIMMONS: Gene Simmons, Sermetel Incorporated. There seems to be a misunderstanding about the possibly proprietary nature of Sermetel coatings. The particular coatings you listed are not proprietary. Within our range of coatings, there is only one process which is proprietary, and that is our 5375 process.

There are a number of classes of Sermetel coatings which conform to the MILC81751 spec. Some of those classes are sacrificial and some are not. I believe there is a good possibility that some of the classes tested were not of the sacrificial variety. You may wish to take a look at some of those in your follow-on testing.

As you pointed out, our coating is designed for high temperature testing and high temperature use, rather than strictly corrosion resistance. But under certain conditions, we have developed a series of chromate conversion type topcoats which helps to seal porocity and extend the life of those coatings. We would hope that these would be included in your follow-on testing.

MR. MEYER: I would like to point out that I never discussed the cost of the system or the coating composition with the vendors. I had only a vague knowledge of how it was put on. I wasn't concerned with that. I was concerned with a product and its performance.

In other words, if the 554 Sermetel were commercially available, it would probably be as useful as the IVD. The only reason we discount the others is that the Sermetel requires a bake which may create problems, and the ether bath has some processing problems. I rank them in order from the standpoint of general, workable processes. I didn't mean to imply that your processes and products were proprietary.

MR. SIMMONS: I just wanted to make sure it is understood that those are on the market in every case.

MR. MEYER: If you have any of these candidates, we would like to get them into the program. We are using the same fastener on the C-141s. We are using a different type of fastener, naturally, on the ground equipment. I have the data and the instructions for those interested in getting test materials on the aircraft or ground equipment. We have places to put them.

MR. GROBIN: Allen Grobin, IBM Corporation. The tin over cadmium coating which AFML pioneered in the early fifties is a very interesting coating system, but it is very tricky to apply. The success of that coating really depends upon the degree of diffusion at the interface of the two metals. A coating can appear very poor in performance if it isn't properly handled. In evaluating that type of coating, you should get involved with the plater and make certain that he bakes the coating sufficiently after plating to get a diffusion zone.

MR. MEYER: We used the mechanically plated tin-cad. The Navy used some tin over cad which was apparently electroplate.

MR. GROBIN: That is what I am talking about.

MR. MEYER: We tested the Ti-Cad, which is a delta process. It was a process developed mainly for landing gears. We didn't actually test tin-cad in our program.

MR. GROBIN: It might be worthwhile to pay attention to the diffusion zone.

MR. COOK: Bert Cook, International Lead/Zinc Research. You mentioned that you were obliged to limit the thickness of the cadmium coating so that you are in the position of comparing 0.3 mils of cadmium against thicker coatings of other materials. Comparison of equal thicknesses is one way of doing it. How about equal cost comparisons? Could you comment on coatings of equal cost?

MR. MEYER: The latest cost estimate comparing cad and the IVD coating was made by McDonnell Douglas about two years ago. They compared the costs per 25,000 fasteners for a particular hypothetical aircraft. They figured a cost of about $5800 dollars for 25,000 fasteners plated with cadmium with the present system. They figured about $8,000 dollars with IVD aluminum, and about $18,000 only if the fasteners were of the 13-5, 13-4 MO stainless steel. If we consider that data to be valid, particularly in the situation where we have many cadmium plating facilities against a rather small base for IVD aluminum, and if they can produce IVD aluminum at that cost with the corrosion performance we have shown, it seems to me we have a very cost effective product.

We frequently come to the point where we can't afford a product. When you have a base price of three dollars a pound for cadmium and thirty or forty cents a pound for aluminum, the base materials costs are going to be less if you can get the process costs down.

MR. JANKOWSKY: Edward Jankowsky, Naval Air Development Center. I just wanted to answer Mr. Grobin's question about Cad-Tin. The coating that we tried was not the conventional Cad-Tin coating. It was a double layer coating with tin on top instead of the normal Cad-Tin which has the tin on the bottom, the cad on top, and then the diffusion. I don't know why it was submitted. Some manufacturer thought it would work.

MR. GROBIN: A number of manufacturers use that coating based on Benny Cohen's work in 1956. For good coating, you need diffusion of the tin into cadmium. That means that as soon as you finish the coating with the tin on top of the cadmium, you must get it into an oven and give it a baking process, or you can get a separation zone. What you want is a three layer system. You want a cadmium layer, a tin-cadmium alloy layer, and a tin layer. Then you have a good system. The baking step does that.

MR. MEYER: In both cases we didn't really pry into how it was produced. We were simply testing candidates.

Evaluation of Alternatives

Session V

Thursday Afternoon 1:45

THE IDEAL AEROSPACE FASTENER COATING

Edward Taylor and John Laurilliard
Standard Pressed Steel Co.
Jenkintown, Pennsylvania, 19046

This paper presents a compilation of fastener coating evaluations and research performed at the Standard Pressed Steel Company during the past several years.

Evaluations and comparisons of many types of coatings were made not only on the effects of the coating on the mechanical and chemical functionality of the fastener and fastener joint, but also on the effects and capabilities of the coating process on the fastener.

Some specific factors considered in evaluating a fastener coating include: corrosion resistance; temperature limitations; hydrogen embrittlement, effects on fatigue life, torque vs. induced load, and stress corrosion cracking resistance; dimensional change; adhesion; thickness and distribution; galvanic compatibility of coating with adjacent joint material; and the limitation of the coating process due to fastener material, size and shape.

The ultimate question of economics is also considered as related to the coating process and the market place.

The determining factors for selecting a coating to replace cadmium as a fastener coating should be related to the intended use of the fastener.

The Ideal Aerospace Fastener Coating

by

Edward Taylor and John Laurilliard
Standard Pressed Steel Company
Jenkintown, Pa. 19046

to be presented at
Government - Industry Workshop
on Alternatives for Cadmium Electroplating
in Metal Finishing

October 4-6, 1977
National Bureau of Standards
Garthersburg, Maryland

INTRODUCTION

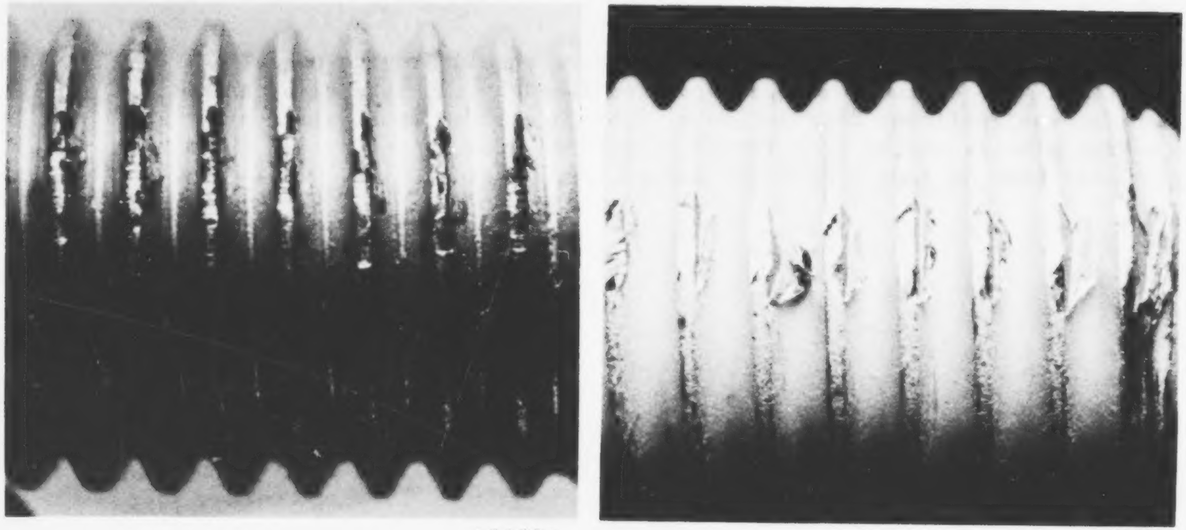
Aerospace fasteners are precision manufactured from alloys ranging from the exotic to the common. They differ from the commercial fastener grades with respect to quality. Coatings are sometimes employed with corrosion resistant alloys, usually to satisfy lubrication or galvanic compatibility requirements. However, coatings are almost always used with alloys which corrode in natural or hostile environments, not only to protect the fastener, but the surrounding structure as well sometimes. This thin coating, measured in ten thousandths of an inch, is depended upon to provide corrosion free protection to a mechanical joint for many thousands of hours.

A threaded fastener appears to be a simple mechanical device. Usually taken for granted, its protective coating is selected to resist a corrosive environment. This simplistic conception does not consider the many critical physical, mechanical, and chemical properties aerospace fasteners are required to have.

Ideally, a coating for an aerospace fastener should provide useful functional properties which cannot be achieved by the bare alloy and will not cause significant degradation of substrate or adjacent structure. The coating process should lend itself to the end product, as well. Let's take a closer look at some properties and process considerations.

Physical Properties

1. Adhesion is necessary to provide reliable protection after mechanical installation. The threads and drive are often scraped, torn, cut or gouged as a result of metal to metal contact. Figure 1 shows the results of good and bad adhesion.



A1860R A1286R

Figure 1. After scraping the threads with a sharp knife, the coating on the left has been cut away. Similar action on the right resulted in peeling of the coating, a condition indicating poor adhesion.

2. Distribution of a fastener coating is determined in order to maintain tolerance control for optimum mechanical and chemical performance. In Figure 2, the thickness distribution of an aluminum coating is shown for an aerospace fastener.

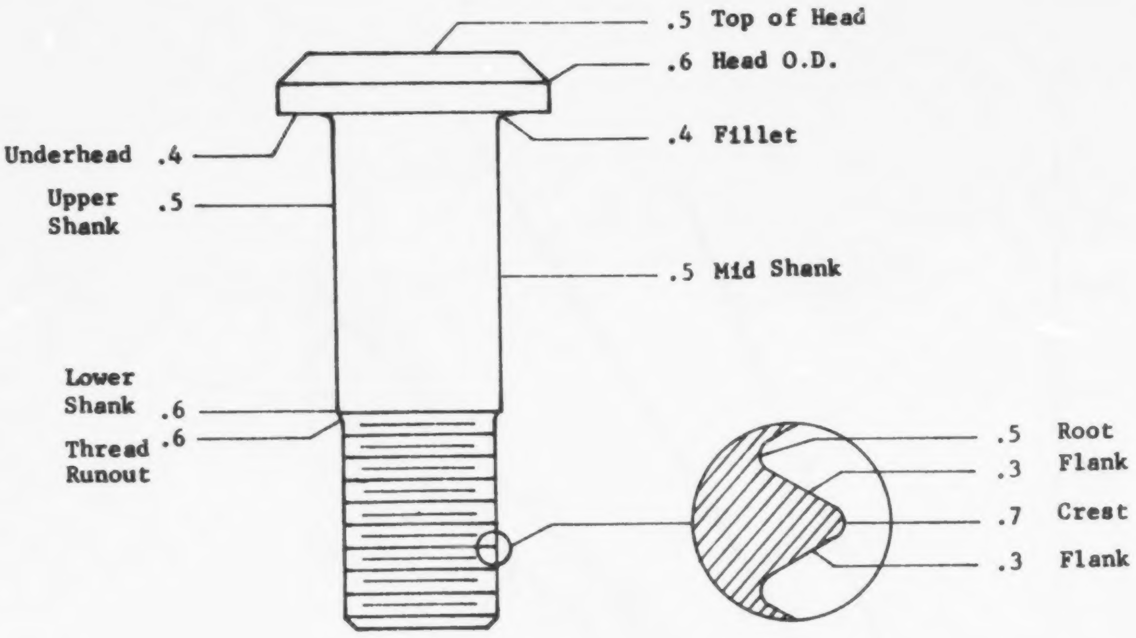


Figure 2. Distribution of an aluminum coating on a titanium aerospace fastener. Thickness in mils, (1 mil equals .001 inches).

3. Cosmetic appearance is an important attribute for aerospace fasteners since it is associated with quality and integrity. Unpainted fasteners must withstand weathering, maintenance formulations and domestic spillage. Fasteners destined to be painted should have a conversion coating which will promote adhesion without affecting mechanical performance.

Mechanical Properties

1. Torque-Tension is one of the most important fastener properties because it describes the quantity of tightening which can be achieved with the joint components and a given amount of wrenching effort.(1) Figure 3 shows how several coatings compared in a previous study.

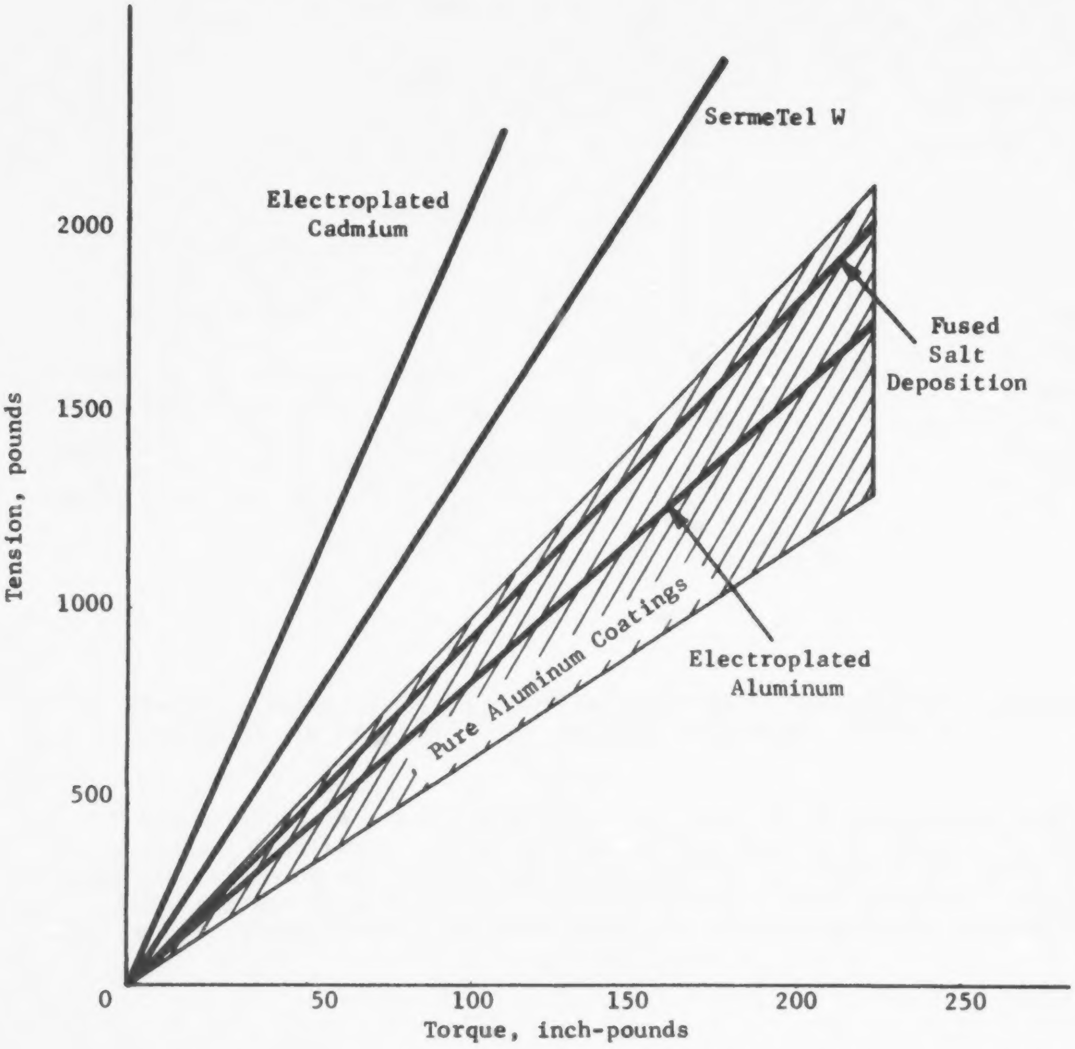


Figure 3. Torque-tension relationship for cadmium and aluminum coated AISI 8740 alloy steel bolts. (No lubrication)

2. Fatigue is a very important aerospace fastener parameter because of the cyclic loading of joints. It doesn't matter whether fatigue degradation is a result of the coating process or the presence of the coating in service.

S-N curves, as in Figure 4 below, show the negative effect of the coating on the fastener at various stress levels. The lack of 2 million cycle runouts for coated bolts at specification load is cause for some concern.

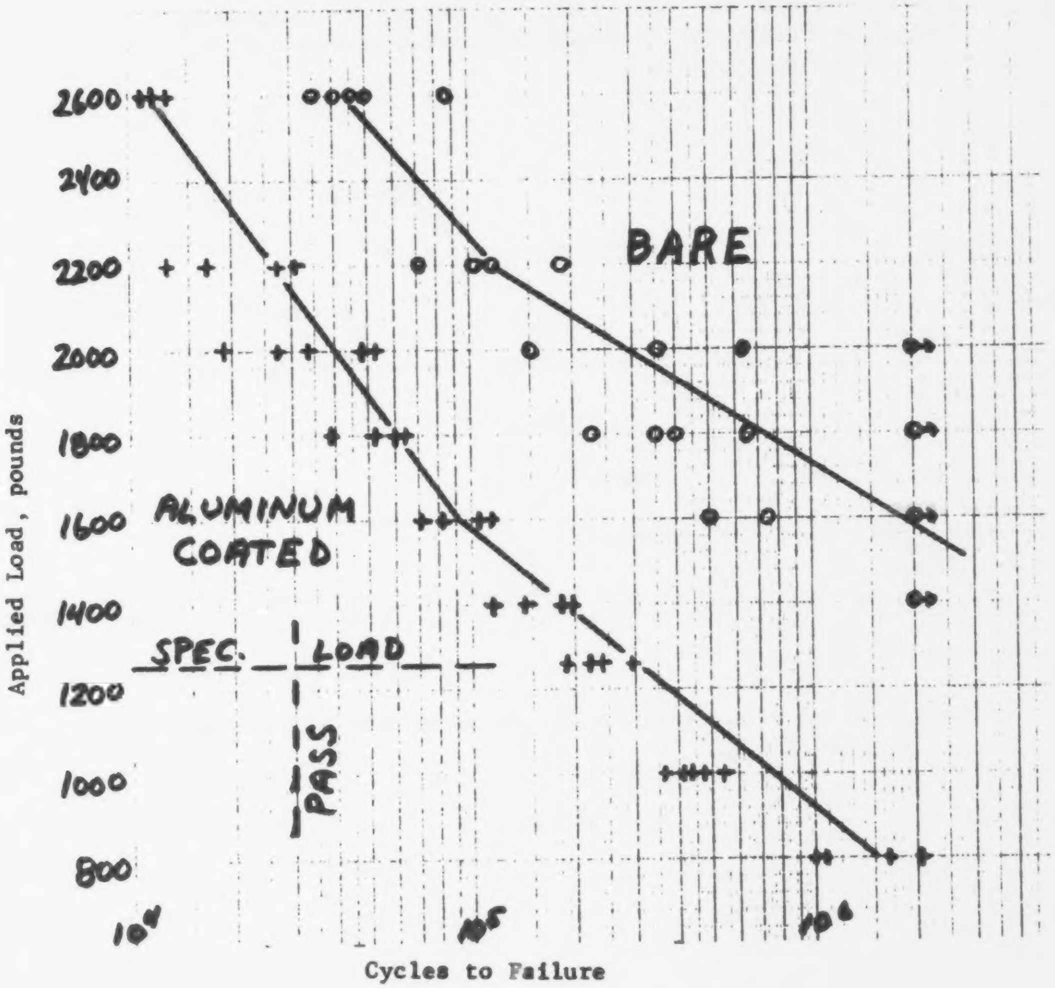
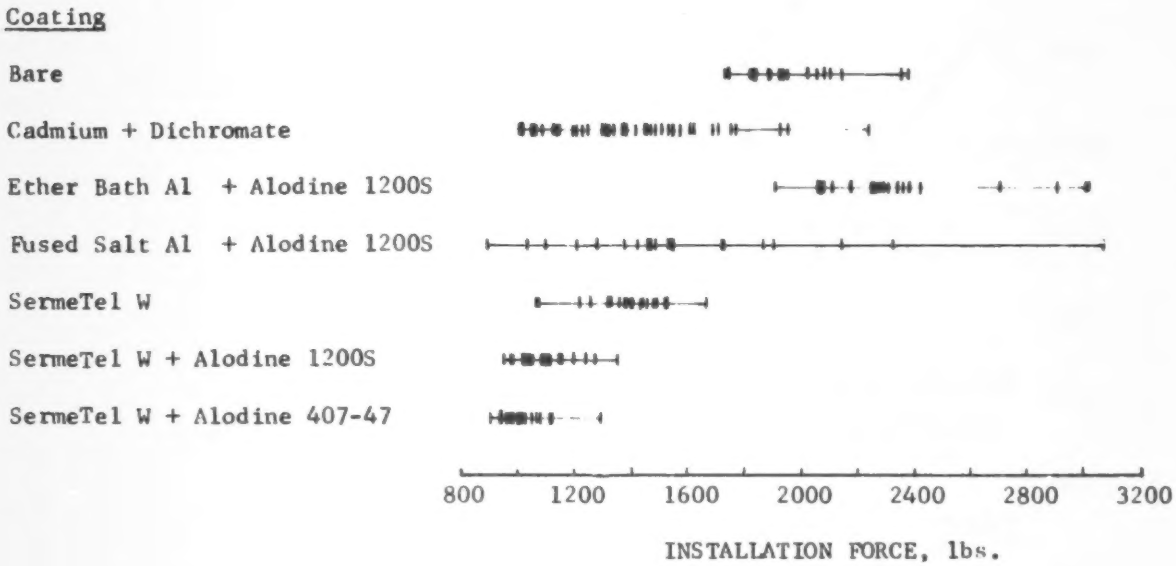


Figure 4. Titanium Hi Lok fasteners (1/4-28, flush head) exhibit the negative effect of an aluminum coating process on fatigue life.

3. Installation Force is required for skin fasteners which have a diameter larger than the structural hole. Lubricants aid the bucking or pounding of these shear fasteners which help structural fatigue life by providing beneficial compressive stresses around the hole. Lower installation forces are normally less costly. Table I shows the results obtained in a previous study.(1)

TABLE I. Force Required for Installation of Coated Titanium Skin Fasteners with 0.004 to 0.006 inch Interference Fit in 7075-T651 Aluminum Alloy.



Note: Cetyl alcohol lubricant employed over all surface conditions.

4. Reusability

Maintenance often dictates the disassembly and reassembly of specific joints. Some joints employ locknuts to prevent loosening caused by vibration. The reusability of these fastening components is normally assumed unless they are mechanically damaged or severely corroded.

Aerospace fastener specifications often require fifteen reuses within a stated torque range. The ability of a locknut to meet this requirement depends largely upon the lubricity of the coating system.

Figure 5 shows the apparent differences in performance by three different coating systems on bolts and locknuts. The absolute value of torque has no real significance since it can be adjusted by the degree of deformation on the locknut. Cadmium provides a consistent installation prevailing torque level while the other coatings exhibit a continuing but comparable percentage decrease. Repeated usage of these fastening systems results in eventual loss of the locking feature and a free spinning nut.

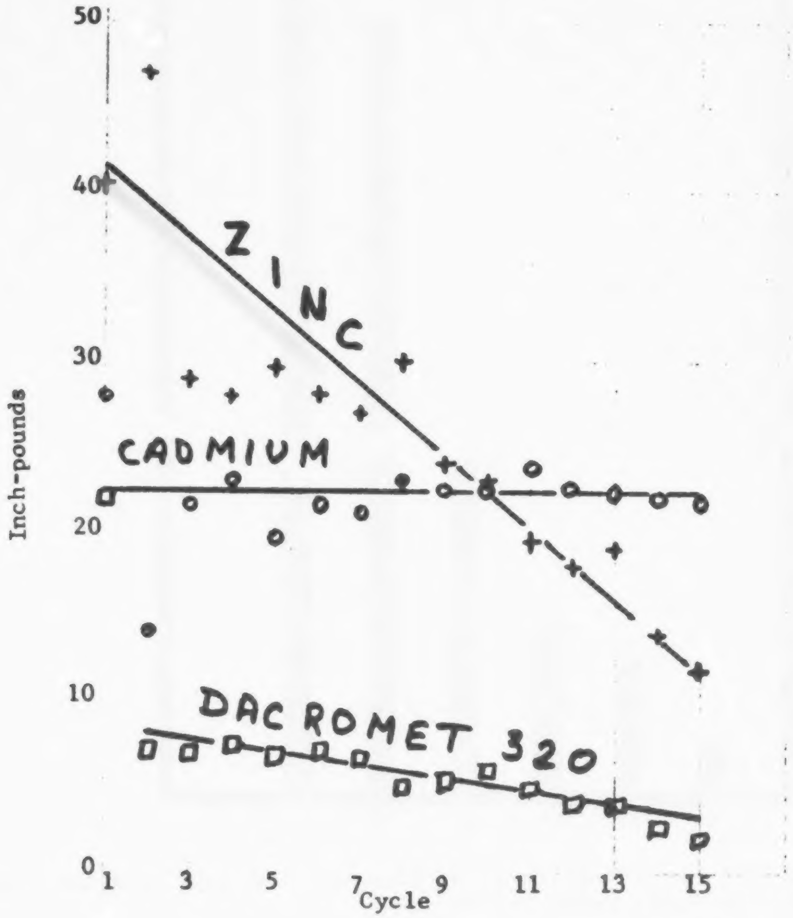


Figure 5. Reusability of three coatings shows different behavior. Fasteners used were 1/4-20x2 SHCS, 20FA-420 Flexloc Nut, waxed. Average of 5 pieces.

Chemical Properties

1. Salt Spray Resistance is an industry wide requirement maintained primarily for quality control purposes rather than to simulate the anticipated service environment. Some coatings are extremely protective in their intended application,(2) but are rapidly consumed in a 5% salt spray cabinet as shown in Figure 6.(1) Until specifications and test methods are modified, freedom from rust in a salt spray cabinet will continue to be a primary requirement for coated fasteners.

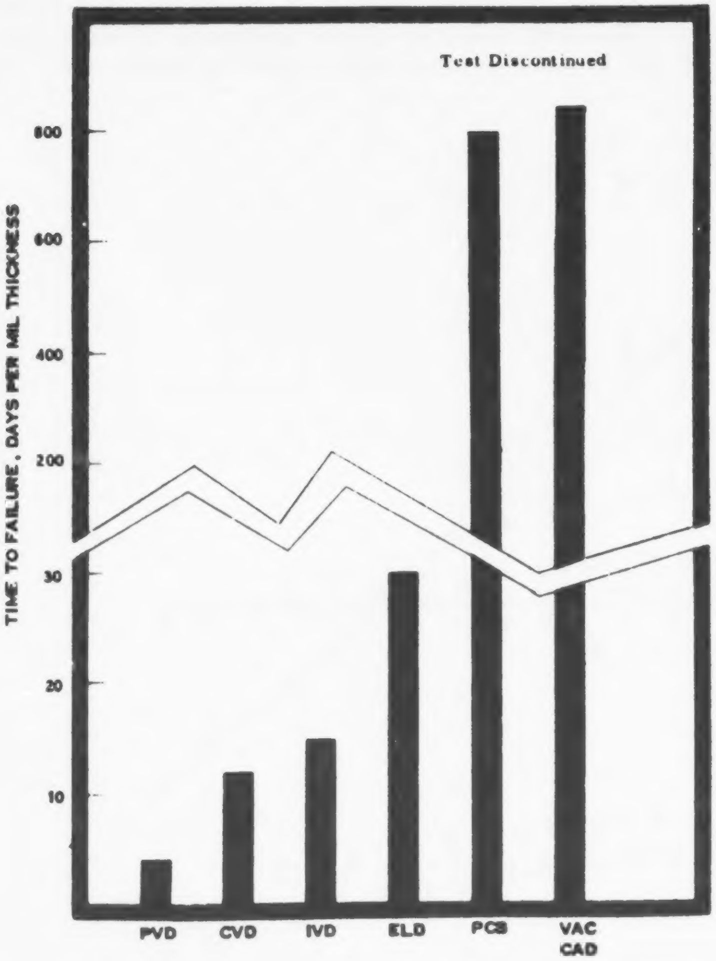


Figure 6. 5% Salt Spray Resistance of Aluminum Coatings on Alloy Steel Bolts.
PVD (Physical Vapor Deposition)
CVD (Chemical Vapor Deposition)
IVD (Ion Vapor Deposition)
ELD (Electro Deposition)
PCB (Phosphate Chromate Bonded)
VAC CAD (Vacuum Deposited Cadmium)

2. Stress Corrosion Cracking resistance is an important parameter for bolts with strength levels higher than 175,000 pounds per square inch. The protective quality of various coatings on 260,000 psi strength level bolts is shown in Figure 7.(3) Noble coatings, such as nickel, have proven to be unpredictable. While sacrificial coatings provide more reliable protection, the best performance is achieved by a combination of noble and sacrificial coatings.

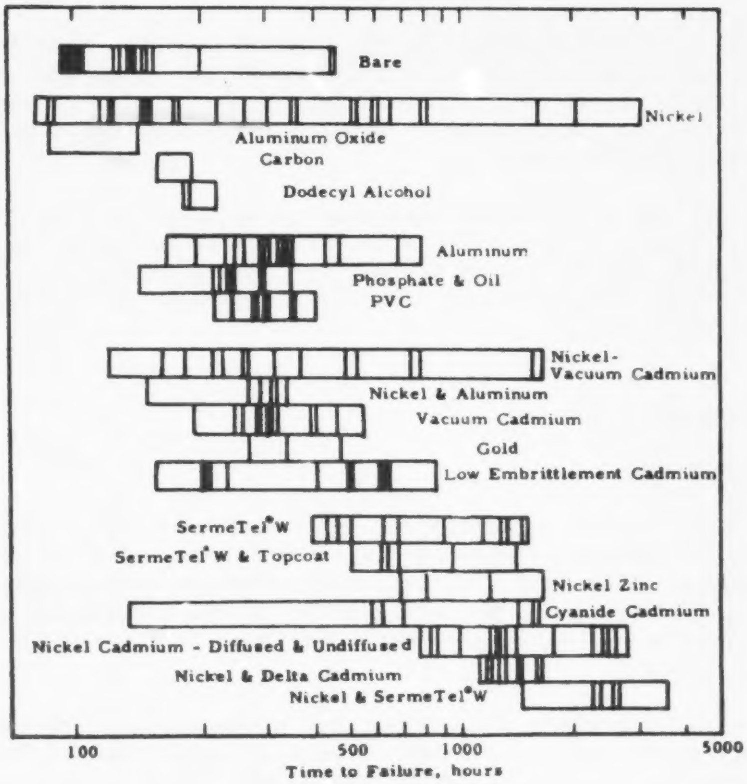


Figure 7. Effect of coating on stress corrosion cracking resistance of H-11 bolts.

3. Hydrogen Embrittlement

Delayed brittle failure of high strength fasteners is usually caused by hydrogen, introduced either from metal finishing or environmental corrosion. The former is well known as hydrogen embrittlement but the latter condition, post plating embrittlement, has recently received increasing attention.

All aqueous electroplating processes introduce hydrogen into the plated object, normally resulting in embrittlement. Relief is accomplished by baking for 3 to 23 hours depending upon the tensile strength, coating type and thickness.

Recent studies have shown bright cyanide cadmium provides superior resistance to post plating embrittlement even though it is one of the most embrittling processes.(4) Conversely, vaccum cadmium causes no process embrittlement, but allows in-service corrosion to produce post plating hydrogen embrittlement.

Although many alternate coatings have been reported to be free from process embrittlement, the ability of environmental corrosion to cause post plating embrittlement has not yet been determined. New candidate coatings, which are very sacrificial, should be thoroughly evaluated in this respect.

Processing for Best Coatings

1. Surface Preparation

Good adhesion is a prime requisite for functional coatings. Fastener coatings must be capable of withstanding some mechanical abuse without flaking, chipping or peeling. Satisfactory adhesion is dependent on proper surface preparation immediately prior to the coating process. This includes oxide and scale removed in addition to the normal oil, dirt and soil removal.

The methods used to prepare the surface for coating should have a minimal effect on dimensions and the mechanical properties of the bolt. For example, acid pickling to remove heat treat scale from a high strength precision bolt is unsatisfactory. It causes hydrogen embrittlement, reduced fatigue life, and a loss of critical dimensions.

Any method of surface preparation that removes more than 0.0001" of basis metal should be avoided, unless it is consistent and reproducible. Adequate removal of soil can be accomplished by alkaline cleaning, but grit blasting is best to remove rust and scale. Corrosion resistant alloys may require activation (chemical or electrochemical) prior to coating to get satisfactory adhesion.

2. Size Limitation

The coating process should have a capability of handling both large and small fasteners with respect to uniformity, quality and adhesion without physically damaging or abusing them. Some processes work very well for large or small fasteners, but not both.

3. Coating Distribution

The ideal finishing process should have the capability of providing a uniformly distributed coating. This coating should be uniform from area to area, piece to piece, and batch to batch. On an individual basis, a minimum thickness must be present in recessed areas without exceeding a maximum thickness on functionally prominent areas, such as the starting thread. If the first few threads of a bolt are over size dimensionally due to excessive coating buildup, the bolt will jam during installation even though the remainder of the threads and the rest of the bolt are dimensionally correct.

4. Tolerance

Aerospace fastener shanks and threads are especially manufactured to very close dimensional tolerances and undersized to allow for coating buildup. A tolerance is required for the variation in thickness from area to area, piece to piece and batch to batch.

Finished fasteners are manufactured to the same close dimensional limits whether coated or bare. If coated, less dimensional variation is permitted prior to coating because some of the total variation allowed on the finished fastener is consumed by the variation in coating thickness.

Coating tolerances are normally 0.0002". This tolerance becomes more difficult to maintain as the nominal coating thickness increases, because of the irregular behavior of electroplating on different surfaces. Whereas the maximum thickness is 100% greater than the minimum for 0.0002" to 0.0004" coatings, this latitude reduces to 66% and 40% for 0.0003" to 0.0005" and 0.0005" to 0.0007" respectively, necessitating close process control.

5. Economics

Initially most alternate coatings will be applied in job shops until sufficient volume is reached, at which time it may be opportune to install an in-house facility. If a high volume cadmium plating facility were the only coating system in a manufacturing plant, its abandonment would require installation of multiple alternative coating processes or force the use of outside coating vendors at increased processing costs.

Assuming a manufacturer can only afford one or two alternate coating facilities, he may have to utilize the resources of several coating vendors. This in turn causes quality problems which increase proportionately with the number of vendors and their physical distance. The costs incurred are significantly higher than for in-house quality control.

5. Economics (Cont.)

Some alternate coating processes are so different from plating, their use requires capital expenditures and increased operating costs. This is because they are sophisticated and require multi-skilled operators and expensive maintenance.

Even though the relative costs for cadmium and alternate coatings are not far apart, the real fastener expense lies in the life installed cost. This takes into account the effect of higher torque and subsequent early damage to head drives and threads; greater number of fasteners due to decreased clamping capability; and corrosion induced damage in marine environments where cadmium is best.

DISCUSSION

We have seen that coatings should provide several of the more critical technical properties described in this paper while being economically compatible with the aerospace fastener. Common coatings comprise about 5% or less of the total fastener cost whereas many alternatives are generally much higher. Even though better, but more expensive, coatings will eventually reduce maintenance expenditures, observation has indicated a continued shortage of purchasing dollars for engineering and maintenance requirements, hence the ever constant disparity between satisfactory and super performance.

Superior coatings will always be in demand for those applications where nothing else will suffice. The less demanding applications present the most perplexing problems because the difference in cost between the common marginal performance coatings and the optimum solution for the job often seems unreasonable. It is only when the costs for maintenance are figured, that the true value of the coating can be assessed.

Although corrosion resistant alloys are now noticeable as aerospace fasteners, the lions' share still goes to plated or coated steel. For these applications, the ideal coating system requires functionality as well as an attractive cosmetic appearance.

A wide spectrum of requirements must be satisfied by the alternative coatings for cadmium, as heavily stressed in this paper. The primary advantage of using one wide spectrum coating for most applications instead of several more specific use coatings is to simplify purchasing requirements and reduce process costs. This concept has universal appeal and will ultimately influence the selection of candidate alternative coatings for cadmium.

The ideal aerospace fastener coating has not yet appeared in the marketplace, but cadmium is still much closer to being ideal than any other commercially available coating system.

If a combination could be made of the lubricity and salt spray resistance of cadmium, the high temperature capability and low toxicity of aluminum, the economy and sacrificiality of zinc, as well as the barrier protection of nickel and chromium, a super coating would result. Perhaps it would be the ideal coating for aerospace fasteners.

REFERENCES:

1. E. Taylor, "SermeTel W Aluminum Coating for Aerospace Fasteners", SPS Report No. 5392, March 24, 1972.

2. F. H. Meyer, Jr. and E. J. Jankowsky, "Corrosion Performance of New Fastener Coatings on Operational Military Aircraft", Paper 115 at 1973 NACE Symposium.

3. E. Taylor, "Stress Corrosion Crack Protection from Coatings on High Strength H-11 Steel Aerospace Bolts", ASTM STP 518, 1972, pp. 131-138.

4. D. Altura, "Postplating Embrittlement", Metal Finishing, September 1974, pp. 45-50.

APPENDIX I

Panel Discussion

"Are Specifications and Standards Barriers to Change?"

Preceding page blank

APPENDIX I

Panel Discussion #1 - "Are Specifications and Standards Barriers to Change?"

Questions

1. Are specifications and standards barriers to change?

2. What role will specifications and standards play in the adoption of materials and processes that are identified as viable alternatives to cadmium electroplating in metal finishing?

3. What means should be adopted for the selection of materials, methods, and coatings for exploration as candidates for use in lieu of electrodeposited cadmium?

4. Many Government and technical society specifications and standards call for the use of electrodeposited cadmium as a corrosion protective coating for hardware.

   What would be the time, cost, and procedures involved in adopting alternative materials, methods, and coatings to replace electrodeposited cadmium in these and related documents?

5. Does the use of materials vis-a-vis performance specifications influence the time and cost involved in changing over from electrodeposited cadmium to potential alternative materials, methods, or coatings?

Panel Members

Mattie F. McFadden,* Raytheon Co./Aerospace Industries Association

Nathan E. Promisel, Society for Automotive Engineers

Walter Conrardy, Air Force Materials Laboratory

John Sarvis, Defense Materiel Specifications and Standards Office

William Quittman, Defense Industrial Supply Center

H. M. Cobb, American Society for Testing and Materials

---

* Chairperson

PANEL DISCUSSION: Are Specifications and Standards Barriers to Change?

At this time, I would like to introduce Mattie McFadden from Raytheon Corporation. She is also with the Aerospace Industry Association and she will be chairing this afternoon's panel discussion, "Are Specifications and Standards Barriers to Change?"

MS: MCFADDEN: I am Mattie McFadden. I work for the Raytheon Company in the Missile Systems Division.

For all too long, I have been in the materials and process business and for the past 20 years in the management of the Materials and Process Department. Three years ago I joined the staff of the manager of Product Assurance in our Division.

By education, I am a metallurgical engineer. By experience, I specialize in all kinds of materials, finishes and processes.

I am a generalist. I am currently the Chairman of AIA's Materials and Structures Committee. For many past years I was active and a Committee Chairman in SAE's Aerospace and Materials Division. I had the pleasure last year of working on a National Academy NMAB study on specifications and standards.

First, I would like to introduce Mr. Nathan Promisel. Nate, would you tell us a little bit about yourself?

MR. PROMISEL: I started my professional life as an electro-chemist, and went into industrial research, in the field of electroplating. Then, as in the case of the Chairperson, I wound up doing all kinds of things on all kinds of materials and all kinds of processes.

This period was followed by some years in the Navy Department in research and development, production control and product control, specializing in the subject area of specifications and standards.

Then followed a period at the National Academy of Sciences where I covered all kinds of subjects, including standards and specifications. I am presently a consultant to industry, universities, research labs, Congress, other parts of the government, and a few foreign countries.

MS. MCFADDEN: Thank you, Nate. Next is Mr. Walter Conrardy.

MR. CONRARDY: I have been with the Air Force Materials Laboratory all of my professional career, which goes back some 25 years. I functioned as a project engineer in both organic and metallurgical materials. My present activity of interest is the role that the Division I head plays in the acquisition of new weapon systems.

We have a key role in approving those materials that will be used in new systems, so alternatives to cadmium are a very vital issue to us. We are in the specification business. We write them. We approve those that other organizations write for use in Air Force systems. We look for alternatives, not only to pollution problems but to the strategic materials question. We are constantly alert to this kind of activity to be sure that the Department of the Air Force is not caught short in a materials crunch by some arbitrary edict that would discontinue the availability of any material.

MS. MCFADDEN: Thank you, Walt. Next is Mr. John Sarvis.

MR. SARVIS: Before my three years with the professional staff of the Defense Materiel Specification and Standards Office, I spent 14 years as an Army Project Engineer in the utilization of materials on small arms and aircraft weapon ordinance.

At the present time, I am with the DMSSO, which is the Secretariat for the Defense Materiel Specifications and Standards Board. Our office is the day to day manager of the Defense Standardization Program, which is the result of Public Law 1028, the Cataloging and Standardization Act.

MS. MCFADDEN: Thank you, John. Mr. William Quittman is with the Defense Industrial Supply Center.

MR. QUITTMAN: More specifically, I am with the Engineering and Standardization Directorate at DISC. DISC is a Defense Department assignee activity on standards and specifications. We review these documents as they are written by the preparing activities such as AFML.

My responsibilities lie in the Federal Stock Class 95, which embraces raw materials. I am not directly involved with plating.

MS. MCFADDEN: Thank you.

Mr. Cobb of the American Society for Testing and Materials (ASTM) is the final panel member.

MR. COBB: Prior to joining ASTM about 12 years ago, I was in industry in a metallurgical capacity, associated mainly with the companies involved with the manufacture of jet engines and nuclear fuel.

In ASTM, we have 128 main technical committees, of which several are involved with electrodeposition and the testing of coatings. The major one is Committee B-8 on Electrodeposited Coatings and Related Finishes. This committee was established in 1945 and now has 150 members, some of whom are in the audience.

The committee has developed about 60 standards, including some 15 or 20 specifications, and some 40 or 45 test methods for determining coating characteristics and recommended practices for preparation of substrates.

This committee, as well as Committee G-1 on Corrosion of Metals, and Committee F-16 on Fasteners, which has a new sub-committee on coated fasteners, are the areas of activity in ASTM which are of concern to the electrodeposition and coatings industry.

MS. MCFADDEN: Thank you. On one hand, we received several questions concerning specifications and standards in general. On the other, we've heard the concern and even frustration that people feel in working with military and federal specifications, and technical society documents. In this aspect, Walt Conrardy and I will engage in a short dialogue to get this discussion oriented. I have several questions to address to specific members of the panel. As we go along, I am sure many of you will elect to ask questions that have come to you as you hear the dialogue.

Walt, you and I have both discussed many times the difference between the two words, "Specifications and Standards".

How do they work? What are they? Who issues them? What is the platform for the words, "Specifications and Standards" as you know them?

MR. CONRARDY: A specification is a device that, within the Department of Defense, is used to describe a material or product in terms of composition or dimensions of geometry. It defines quality standards and levels that are the minimum that the DoD will accept when we procure something. It includes test methods. It describes ways of determining that quality, and it provides some packaging and transportation instructions or intended use information at the end.

Specifications usually identify deliverable end items, whether they be materials or "widgets." Standards, on the other hand, are more philosophical documents describing acceptable and unacceptable practices for specific manufacturing, chemical, or metallurgical processes, such as electroplating or heat treating or shot peening.

Specifications create a great deal of frustration for people, since it is difficult to elicit the complete agreement of everybody on any given spec. Everybody has his own point of view and axe to grind, but specs represent compromises between the vendor and the user that reflect at least the minimum needs of both, and that one agrees to provide when the other one so orders.

They are slow in evolving, and they are slow in getting changed unless some crisis situation precipitates some fast action. We will probably get into some of that procedure if we go on with this discussion in terms of whether the specifications are or are not barriers to introducing alternatives to cadmium.

MS. MCFADDEN: Depending on the origin of the document, some organizations, groups, or agencies elect to call all their documents standards. It is a group that defines a standard; as in ASTM, American

Society for Testing and Materials; as in SAE, Society for Automotive Engineers; AMS or Aerospace Materials Specification.

This morning in one of the papers there was a slide that listed some specific ASTM and AMS numbers relating to cadmium. They didn't list QQ-P-416, which is the Federal cadmium plating standard.

I would like to address one of the questions that came up, "What will be done about MS specifications," it says, "requiring cadmium on fasteners for military, particularly Naval applications?"

MR. CONRARDY: When a new process is introduced which has been sufficiently characterized with a data base adequate for writing a definitive spec, the obvious way to get that new product into use is to describe it in a specification. The mere issuance of a materials spec or a process spec does not get this new process in use immediately or over a substantial period of time. A process that is applied to some end item is described in its own specifications or drawings.

The MS sheet that Mattie referred to is a single page. There are literally hundreds of these in the military system specifically describing fasteners. All kinds of fasteners with a variety of thread sizes and shank diameters and head recesses and thread pitch, and numbers per inch are described.

Each one of them describes the material composition that applies to that fastener, and includes a description of the kind and amount of protective coating that will be put on that fastener, so it is easy for the materials community to issue a new spec. The Air Force did that about a year ago on IVD aluminum. But you can't go out in the marketplace, except perhaps in St. Louis near McDonnell, and buy any IVD aluminum on aerospace parts. The industry is not geared up to provide it, and it will be sometime before this is available.

In addition, the individual MS sheets which procurement people cite when they want to buy something have to be changed. If we elect to use some alternative to cadmium, that has to be so noted on that drawing and the drawing reissued. Then, when procurement people reference it, they can require some coating other than electroplated cadmium.

Hardware items are not controlled by the materials people, nor by corrosion engineers. That expertise resides in the Air Force Materials Lab. The people who buy and manage the hardware are elsewhere. There is a tremendous logistics problem of identifying all of the other documents that call for a specific process, for example, electroplated cadmium, and getting each one of those changed.

We can't do it by edict. You have to go to the individual who is responsible for that particular end item, determine why he needs a particular coating; and then select the best alternative for his item and have that document changed.

There is a very large number of MS sheets and it will be a substantial job to get them all changed. In that sense, specifications could be a barrier. Given the resources to do all of this, they need not be a barrier.

MS. MCFADDEN: That brings up an interesting question that I would like to ask of John Sarvis and of Nate Promisel.

John, is there an inter-agency time-table that has been established to eliminate cadmium specs by way of substitution of alternate? Is an edict from high above required to make government and industry move?"

MR. SARVIS: On the first question about an inter-agency timetable for eliminating Cd specs by substitution of alternative means, I am not aware of any inter-agency date for such elimination. From what I have heard here over the past two days, it may not be advisable to come out with a date for automatic elimination of all cadmium in the specifications for all items. There may be a case-by-case basis where we might want to avoid such things.

Is an edict required to make the Government and industry move on this? No. Our office, the Defense Materiel Specs and Standards Office, communicated with Deputy Assistant Secretary Marienthal's office some months ago on the problem of fluorocarbons. Our office is in the process of inquiring about the use of fluorocarbons in items used by the Department of Defense on which it has specs.

So an edict isn't required. We are already doing this in the case of fluorocarbons in DoD. I am sure we will be doing it in the case of cadmium, not necessarily to eliminate everything that contains cadmium, but to make an investigation of what is entailed in its use.

Perhaps I should refer the industry portion of the question to Mr. Promisel.

I don't know of any timetable, and I would really be surprised if one emerged except perhaps in the form of a target or a goal, but not a mandatory affair at this stage.

In terms of edicts, this is not in line with Government operation and Government activities. Such a situation could occur in the industry, however, through stricter controls being mandated which would then, persuade industry to voluntarily change its practices. In this context I think an edict from EPA or some other source may indeed accelerate some action in both industry and government.

I think the spec writing societies such as ASTM and SAE are well aware of the risks of cadmium pollution. Even two or three years ago, the Aerospace Materiel Specification Division of SAE began to take a hard look at specifications to see what they could introduce at that time, anticipating problems not only with respect to safety and health, which is the main consideration with respect to cadmium right now, but also with respect to critical materials. SAE and the other societies would be very cooperative and very anxious to help do this on a progressional, rational, realistic, economic and safe procedure. I think we can expect full cooperation from outfits such as SAE.

MS. MCFADDEN: Mr. Cobb, would you like to comment on the position ASTM might take?

MR. COBB: I think it is important to keep in mind that when we refer to ASTM or SAE we really mean the people from industry, Government, and universities who are members of these committees. What needs to happen will happen. If a group of people need a new document or a revised document, they come together at the meetings and they produce it.

MS. MCFADDEN: There was another question related to this. It says, "Does the DoD specify cadmium plating for all hardware exposed to the environment; that is, marine environment, upper atmosphere and so forth?"

MR. CONRARDY: I think we could flatly say no, we do not require everything to be coated with cadmium or this would be a cadmium world. A battleship going sailing down Chesapeake Bay with one great big gleaming coat of cadmium plating -- obviously, this isn't true.

Any weapon system is an assembly of its individual parts and components. When each one is designed, a drawing is issued that gives its geometry and its tolerances, and includes the materials with which it is constructed. A finishing system is specified to provide any particular functional purpose that may be required, whether it is chrome plating for hardness on bearing surfaces or cadmium plate for environmental resistance. These things are usually reviewed by materials engineers or corrosion engineers, as appropriate, to judge whether the right material and process were selected to ensure that it will survive for the timeframe that the Department intends to use it.

Through experience, we have learned that if an aircraft is designed for 15 years, we look for processes that will keep it flying for 30 because that is the way we utilize our equipment.

There is no arbitrary overall policy that says, "Everything in a marine environment will be Cd-plated or any other kind of process."

It is looked at on a piece by piece basis. Undoubtedly a philosophy that says, "Very serious consideration will be given to corrosion resistance," and it will not be an after the fact bandaid type operation to try to make it work after you slip it off the drydock.

The Navy is very corrosion conscious, and they select basic materials and finishes with a very aggressive environment in mind, but this can take the form of many different materials and processes.

MR. PROMISEL: Just to underline the negative answer to that question, there are in fact places where cadmium is forbidden and prohibited from being used, depending upon the technical considerations such as temperature restraints and cadmium contact with titanium under certain conditions. Not only is it not mandatory universally, there are cases where the use of cadmium is not permitted.

MS. MCFADDEN: Thank you. Following up a bit on your comment, Walt, if anything was done to reduce the usage of cadmium, would it be retroactive on existing drawings, or would it affect only new designs?

MR. CONRARDY: I would envision an action requiring all new systems not to use cadmium. Then might come new specs and new standards for new finishes. In an evolutionary sense, this could take place over a number of years, and all of the hardware that is now in the field and has parts with cadmium finishes would remain that way.

MS. MCFADDEN: So nobody is going to ring the chimes at midnight and eliminate cadmium?

MR. CONRARDY: I can't imagine that happening.

MR. QUITTMAN: There are 18 Federal Stock Classes that we are responsible for at DISC, including a variety of items: nuts, bolts, screws, washers, and bearings. Many of the specifications that cover these items have an alternate protective coating or an alternate material.

In the smaller hardware items, you have these options. Alternatives could be specified in a contract or a purchase description or something like that, and you could eliminate or reduce the usage of cadmium. You wouldn't have to start fresh and write a new specification.

MS. MCFADDEN: In other words, there are documents for some of these finishes, and then there are some finishes that haven't yet been documented.

MR. PROMISEL: Walt, what would be the possibility of the Air Force, the Navy, or the Army issuing a document, making it permissible to modify contracts under certain conditions and for certain applications to specify the use of alternatives to cadmium where appropriate, necessary, convenient, and practical on old systems?

MR. CONRARDY: I think that would be a very constructive way to encourage the change on a broader basis.

As I indicated earlier, our aircraft have a very long life. That means they get overhauled many times during their lifetime. Some of those overhauls are extremely detailed in their disassembly, right down to removing individual fasteners to treat corrosion.

We are doing a complete tear-down, for example, on C-131 wings right now that goes all the way to the removal of the last fastener. There is an opportunity to reassemble the wing with whatever new and approved schemes are practical, cost-effective, and help alleviate any environmental problems.

MR. PROMISEL: Mattie, there are two numbers which might be impressive. One is that there were about 4,000 specifications on materials and processes listed in the DoD Index of Specifications and Standards. There are just about that many non-Government standards. Therefore, we are talking about maybe 8,000 pieces of paper not counting the drawings that Walter mentioned originally. Not all of these are related to cadmium certainly, just a small percentage. However, you can begin to see what a tremendous area we are dealing with when we are talking just about materials and processes.

We all know that in mass production pulling something out of the line and putting something else in is costly. From my company's point of view, we would feel very strongly about that, especially if we had to absorb the costs. We would be very much against it.

On new design coming up or physically reworking an item that I can hold in my hands, yes, I can see it on that basis, but on an automatic production run, I find that very difficult.

MR. CONRARDY: As Nate indicated, it would be done on a voluntary basis, and I suspect that a lot of end users might want to do it, even in ongoing production. At least some would use it to develop their own experience with this new alternate and develop vendors and suppliers so that when the switchover comes, they will have these people all lined up.

MS. MCFADDEN: Yes, I can see that point. There is a gentleman there that has a question, yes?

MR. BOOKER: I am John Booker. Since you are talking about changing over standards, is there a systems approach that can be used in changing coatings, or is every individual item considered? For example, an aluminum screw on a stainless steel panel on an airplane resulted in the airplane being overhauled after two years rather than after five years as scheduled. They repaired it with a different part, but every new plane produced still had the aluminum bolt on the stainless steel panel. Is there a way of changing such components or coatings during production runs? From what you said, that would be almost an impossible task.

MS. MCFADDEN: There are changes every day in production lines. I think we know this. In my case, I was referring to a plating system that would be replaced by something else that probably would require a totally new finishing system.

It can be done, but it would be much more costly than to replace a fastener which is an item that doesn't involve a lot of equipment. You generally purchase it rather than buy the machines to make the the fastener.

It is much simpler to switch a fastener than it is to switch a plating process on the shop floor, but both can be done. It depends on how much money you want to invest in doing it.

MR. CONRARDY: There are a few examples of what you mentioned. When we buy a new weapons system, the drawings are prepared by the contractor who builds it. In the case of the F-15, for example, McDonnell designed it and they prepared drawings of each piece of the aircraft, and they specified the finish that is on each piece. This was done by the original design engineers. Two years later, after the aircraft is out of production, it becomes a chronic maintenance problem for the Air Force because the proper engineering expertise is no longer available to identify any problems in design and recommend a substitute material. The point is, you never get back to the engineer who specified the coating in the first place.

MR. WILSON: Verner Wilson, 3M Company. Recently, a certain Northeastern city stated that no more Cd could be plated in their particular city. I don't know if it was just a ban on Cd plating, or if Cd effluents were limited. However, it was clear that there would have to be zero discharge of cadmium to the municipal waste treatment system.

Are you familiar with this?

MR. LAURILLIARD: Due to their license for dumping sludge in the Atlantic off of Maryland, Philadelphia has had to reduce heavy metal content of their sludge, particularly cadmium.

The Water Commissioner concluded that the cadmium in the sludge came from electroplating shops.

In Philadelphia, there is not much waste treatment or treatment of the rinse water other than maybe some type of acid neutralization step Whatever heavy metals are in the rinse water go down to the municipal waste treatment plant.

Plating shops that can keep the Cd metal below about one tenth of a part per million are allowed to continue, but since they don't have any waste treatment, it would be difficult to reach that low limit.

MR. WILSON: What do our standards and spec people do if Philadelphia bans the plating of a certain metal?

MR. CONRARDY: For the time being, at least, it is fortunate that Philadelphia doesn't constitute the world. You can run over to Wilmington, Delaware, or you can run up to Brooklyn, New York. I am sure there are other job shops that could take care of it, but that is only a symptom of the problem. Perhaps we will see this more and more as time goes on and as people become aware of the pollution problem that is occurring.

I am sure it is an inconvenience for people in the Philadelphia area who have been depending on those job shops, but those kinds of edicts are unpredictable. The only thing I would predict is that they may occur more frequently. Philadelphia wouldn't have acted if somebody hadn't threatened them with a pile of solid waste that they had no place to put.

MS. MCFADDEN: Before I take any more questions, there are two written questions that were turned in. I would like to address them.

One question addressed to me says, "Does your company or the Association you represent foresee any critical usages of cadmium in the aerospace industry, particularly for electrical or electronic purposes or functions?"

In answer to this question, the Materials and Structures Committee of AIA distributed the questions that were prepared for the panel to our members, one person from each of the major aerospace companies, to express their opinions, and we collated that. The National Aerospace Standards Committee of AIA also polled its members and some fastener vendors. You may obtain copies of these reports from Jack Reese or myself. (AIA REPORT IS AN APPENDIX IN THESE PROCEEDINGS)

Someone remembers World War II stockpiles, as I do, and many of us here do. Will the Government maintain a strategic stockpile of cadmium for defense purposes?

MR. QUITTMAN: This is a possibility, because these materials might have a specific use, and therefore, they would be stockpiled

MR. CONRARDY: Yesterday somebody showed a pie chart that described the principal uses of cadmium. This included nickel Cd batteries, pigments, and stabilizers as the major uses, in addition to electroplating. Certainly, for nickel cadmium batteries alone I believe the Government would in fact continue to stockpile cadmium. We use a great deal of nickel cadmium batteries in aircraft systems. Of course the bulk form largely does not represent as serious a pollution problem. It is in the use of cadmium as a protective coating where most of our problems are introduced.

MS. MCFADDEN: Mr. Cobb, would you like to give any last minute comments on our topic?

MR. COBB: I don't look on standards and specifications as barriers to change. Standards are agreed upon ways of doing something, buying a product or performing some task. Standards and specifications are necessary in buying a new product or modifying an old one. It seems to me that the standards-writing community must keep abreast of the new needs of the industrial community and prepare those documents that are needed.

MS. MCFADDEN: Thank you. Walt, do you have any summary comments?

MR. CONRARDY: AFML has been looking for alternatives to cadmium because fasteners in aircraft structures are the single biggest source of corrosion problems. We have had this problem for many years with cadmium. In his paper tomorrow Fred Meyer will describe the field experience we have obtained.

As these things evolve, we write and issue specifications. IVD aluminum may be used as an example to facilitate the procurement and general introduction of new processes.

Specs, then, are not a barrier, but they facilitate the entry of a new material or process. I think we will see an increasing use of alternatives as time goes on. We will gradually decrease the amount of electroplated Cd used for both performance reasons and pollution reasons.

MS. MCFADDEN: Thank you. John, do you have any further comments?

MR. SARVIS: I wonder if this question should actually read, "Are specifications and standards vehicles to change?" In truth, a specification is an authorized description of something that works. This means that a certain amount of testing has to be done to make sure that it works under those conditions in which it must operate.

The standards of course are agreed-upon engineering limitations. I would say that a specification tends to be at the end and is perhaps the goal of development in that we need to express its culmination on a piece of paper in order for the procuring contracting officer to buy it.

We could say that specs are vehicles for change, operable only when the development people have done their homework well.

MS. MCFADDEN: Thank you. Nate, do you have further comments?

MR. PROMISEL: I certainly do not feel that specifications and standards are barriers to change. I think intrinsically they are not. Here and there you may stumble over a transient obstacle, but basically they are not barriers, and the obstacles in time, of course, will be removed.

One of the bigger problems, perhaps, is the timing aspect of it. Can specs, standards, and directives, be changed in a very short order? Sometimes, that is one of the obstacles we encounter. It takes a little longer than some of us would like to see, but again it is only a transient situation, by no means a barrier in any true sense.

I think there are some very positive aspects of specifications. They can contribute to the objectives that are desired in introducing changes. They can contribute to health and safety, aspects that weren't fully addressed years ago when health, safety and pollution were not matters of concern in specifications.

They can contribute to conservation through introducing substitutes and interchangeability. They certainly can contribute to environmental protection.

They can serve as documents to identify new techniques which are advantageous in terms of all the things I have mentioned and even economics. There could well be economic incentives. Sometimes you want to change when you recognize what the new techniques can offer.

Of course, they serve as a mechanism for certifying -- I am not sure that is the correct word -- new processes and new materials which can be used and sometimes perhaps must be used.

Then there is a section in specs on notes. One can put a lot of very good and useful information under notes which serve as a guide. They are not mandatory requirements, but they are very helpful and can serve as a guide.

There are a number of very positive things about specs. It isn't just a question about the quote, "barriers."

MS. MCFADDEN; Thank you gentlemen. The panel is adjourned.

APPENDIX II

Panel Discussion

"How Essential is Electrodeposited Cadmium?"

APPENDIX II

Panel Discussion #2 - "How Essential Is Electrodeposited Cadmium?"

Questions

1. Are most alternatives to electroplated cadmium available today?
2. What is the economic significance of electroplated cadmium?
3. What would be the economic effect of removing electroplated cadmium from the market?
4. What is the environmental/health significance of electroplated cadmium?
5. What would be the effect on the "quality of life" in the U.S. resulting from no longer having electroplated cadmium available or using an alternative product?
6. For what applications of electroplated cadmium are there no alternatives?
7. What alternatives to electroplated cadmium were not covered in the Workshop?

Members

Martin White, Cadmium Association

Gerald Kraft, Kraft Chemical Company

W. E. Snyder,* Metal Finishers Association of Southern California

Albert R. Cook, International Lead Zinc Research Institute

Allen W. Grobin, Jr., IBM Corporation

J. Laurilliard, Standard Pressed Steel Company

---

* Chairperson

Panel Discussion: How Essential Is Electrodeposited Cadmium?

MR. DYCKMAN: This afternoon's panel will address the questions that EPA may ask in the future concerning the essentiality of cadmium.

A letter from the National Association of Metal Finishers, has been distributed to you at the Workshop. It makes the statement, "We, the National Association of Metal Finishers, believe cadmium is essential." However, it is not enough to believe in essentiality, you have to prove it. This panel will go one small step in that direction.

I would like to introduce our panel chairman, Bill Snyder.

MR. SNYDER: Let's introduce the rest of the panel members: Martin White from the Cadmium Association, Allen Grobin from IBM, Bert Cook from the International Lead Zinc Research Organization, and John Laurilliard from SPS. I am Bill Snyder from the Metal Finishers Association of Southern California. I am an electroplater.

I would like to address the question, "Are most alternatives to electroplated cadmium available today?" From the standpoint of the airplane plater, until any proposed alternative is qualified by a prime contractor (I define prime contractors as Boeing, Douglas, et al.), it isn't available to use on their hardware.

Qualification historically has been both expensive and time consuming. The prime contractor has to involve his process, his engineering, his design engineering, his quality engineering, and his procurement people in attempting to qualify a given process. He may then elect not to permit its use until each individual supplier has been qualified.

We do some fairly large fasteners, and I've heard a lot about small chamber barrel type coatings at this workshop. I pose for your consideration the following. My shop may receive three to four pieces at a time of a main landing gear drag brake. This part is approximately four and a half feet long, eight and a half inches wide at an eye-beam section. It has a bearing bore and a neck down face on each end. In the web section there are a lot of deep pockets.

A typical plating requirement would be two to three tenths in the bearing bore, three to five tenths on the bore face, seven tenths minimum all over. I am not sure that I have heard an alternative material and process at this workshop that will handle that.

We have talked a lot about increased thicknesses, and I haven't heard much discussion of weight. I will guarantee you that in the airplane business and more particularly in the aerospace end of things, weight is a rather vital consideration.

I think right now I would like to ask Al Grobin if he has any comments on that.

MR. GROBIN: On a number of specialty items, the alternative to cadmium plating would have to be very carefully studied. Keep in mind that some three hundred or four hundred lives will depend upon the ability of that substitute to do what cadmium does today. On the other hand, we have a lot of other hardware which can be readily substituted. So we have two ways to go. I think it is up to those of us who do not have hardware that has a life dependency to start the ball rolling and gather the experiences necessary to qualify these alternatives before the airplane people.

The advent of a problem has just come about. It is going to take a long time to qualify alternative materials.

MR. SNYDER: The question was asked, "What would be the economic effect of removing electroplated cadmium from the market"? I would like to change that to, "What would be the economic effect of going to the alternatives"?

I believe it is the consensus, from what I have heard in the last few days, that no single proposed alternative will replace cadmium totally. Thus, we have a situation where platers may be required to install two or more processes to replace one. That is going to be difficult, if not impossible, due to a few operating restrictions that we platers are laboring under.

Most of us by now have sewage discharge permits of one form or another. I can't speak for the rest of the country, but in Southern California the permits make it clear that you don't put any more tanks in. You can take one out and put another one in, but you don't add any process.

We have air pollution control permits. At the moment, we can still add to those. There is considerable expense involved, but as far as the air people are concerned we can still expand our facilities.

Many of us have energy problems. Our local power suppliers don't want us to add another substation. Many of us have fuel quotas. Many of us, and particularly in Southern California, have water use restrictions. Thus, the installation of alternate processes may not be possible. If it is possible, it will always be expensive, and I would mention to those of you from the governmental airplane users to think one thing. As an electroplater, I may be about the sixth man down the tier in the production of a part. If I must add fifty cents a part to cover my increased operating costs, by the time you get to see it, it is going to look more like $3.75. Everybody in each tier up is going to take my fifty cents and put his percentage on it. You are going to have some expensive aircraft.

MR. WHITE: I wonder if I may comment on where we should look for economic benefits or economic losses.

First of all, it is often forgotten that cadmium is produced by zinc producers. Cadmium brings in profits. The zinc price is very depressed at the present moment and not being able to sell their cadmium may be the straw that breaks the camel's back. The zinc producer has to be able to sell his cadmium.

You also have to look at the man-hours spent in devising and testing new specifications. We have all heard that salt spray is not the answer. You have to do in-service evaluations, and that takes time and man hours. I think there is almost a need for a specification on how to compare coating techniques, because everyone is busy comparing them using different criteria.

Of course, you have a loss of materials due to corrosion, if you are going to put up with a material that doesn't give you the same service life. You have increased imports of costly materials. You heard this morning how much cadmium is imported into this country. I think this is true of a lot of other materials. You have to be very careful not to run up a very large import bill by making the country very dependent on another country for the supply. You have investments in new plants. Some of these alternative techniques are just great, but can the small plater afford them? If he can't, what is going to happen to his employment situation?

Finally, you must consider energy. I know that the U.S. government is very well aware of the energy problem. I think that several of the processes we have discussed require considerable energy input in terms of heat or electrical power. I think all of these things have to be considered and not just the question of how much does this particular component plated with cadmium cost, compared with Sermetel.

MR. LAURILLIARD: I get the feeling from talking to a few of you that you are really not well aware of the significance of high strength fasteners. Fasteners are normally the last thing to be considered when you are making an assembly. At the last moment, a rush order is put in, or somebody runs down to the hardware store to get whatever they can to hold the assembly together.

I guess it is because fasteners, nuts, and bolts are so relatively simple. Can you imagine anything simpler than a bolt? Except maybe a safety pin or a straight pin. When you get to the field of high strength fasteners, the uses are normally in critical applications. These are applications where life is at stake. If you could just imagine for a minute that all the fasteners in the world disappeared, you could imagine cars blowing apart, bridges blowing down, and airplanes falling out of the sky. You can see that fasteners do have some very critical applications.

What we are selling or buying in high strength fasteners is clamping force or clamping ability. The clamping force, the tighter that we can clamp a fastener or clamp a joint together, the better that joint is going to be in resisting failure due to fatigue or looseness. When you are at 30,000 feet in an airplane, and you look out the window to see the wing flapping up and down, what kind of fasteners do you want holding that wing on? When you are landing, what kind of fasteners do you want holding that landing gear on? In those critical applications, I don't think we should substitute a coating that will not give us what cadmium will give.

MR. SNYDER: I want to digress just a moment to what I picture as the original reason that this conference took place. I don't think we are here to explore technology for technology sake. If you will recall the letters announcing the conference, the topic dealt with the toxicity of cadmium. We have heard about its impingement upon the food chain.

Recently the State Department of Health in California put forth a proposed limit of 25 parts per million of cadmium in the sewage sludge if that sludge was to be used as a soil amendment agent for agriculture. Now this limit was put forth on an informal basis. In response, the Metal Finishers Association was fortunate enough to avail themselves of the services of a data link base at USC.

Through that data link we got into the data bases of NASA and the Department of Agriculture, Department of Health, and four other data bases. We extracted a list of well over 400 documents that have been written in America, Japan, Germany, and the U.K.. We then obtained a consultant to evaluate these documents.

We presented a summary report of the State of California and they withdrew their proposed guidelines. They are seeking now to go another route. I would like to quote briefly from the report that we presented to the State of California. I want you to remember that there was no original analytical work done here. This is a paperwork report. We took the available literature, we read it, we evaluated it, we set down what we thought we saw in it.

The comments are as follows: "Cadmium uptake by plants is much more complex and the extensive literature accumulated appears to be very confusing and contradictory indicating insufficient knowledge. Cadmium uptake by plants appears to be related to pH of the soil; soil texture; microbial action in the soil; concentration of other heavy metals; available phosphorous and/or nitrogen; method, frequency, and loading of sludge.

"Again, the problem regarding cadmium is very complex with contradictions appearing in the literature. These are due in part to insufficient knowledge or control of experimental parameters, and even the methods used to analyze cad contents of such low concentrations can be doubtful and suspect, as indicated by the WHOFAO report." I believe we heard mention of that report and its comments on analytical capabilities by a gentleman from FDA.

I would like to quote from "U.S. EPA Guidelines on Sludge Utilization and Disposal. A Review of Its Impact on Municipal Waste Water Treatment Agencies," Report Number

75-20, Municipal Sanitation District of Greater Chicago. The report was published in October 1975.

"The actual conclusions presented are: (1) U.S. EPA proposals were not supported by current and available relevant research and full scale data. (2) Proposals have seemingly ignored data generated by their own organization and by other organizations. (3) Proposals are based on the assumption that metals will accumulate to harmful levels in the edible parts of plants. This assumption is not supported by available data."

Copies of the report that I mentioned can be obtained from the California office of the Metal Finishers Association. A bibliography is included in each report.

MR. COOK: I would like to look at the more general picture here. I would like to congratulate Ed Dyckman and the Steering Committee on bringing together this type of conference. It has been very enjoyable and very instructive to all of us. I would, however, suggest some improvements. One improvement would have been to hold this conference considerably earlier in the decision making stage of the proceeding. Another improvement would have been representation on the Steering Committee by industry and by overseas delegates, perhaps NATO, to bring in a world picture. I think these are important points for any other materials that may be dealt with in this manner in the future.

We are all equally concerned with the environment. We all want to see safe operations. It is up to the United

States government to issue regulations to insure safe operation. These regulations will have an economic impact on cadmium plating.

If that economic impact is such that other alternatives come to the fore, then the cadmium plating industry would defer to that situation. However, it seems to me that because of the feeling that cadmium is toxic under the circumstances of use, then decisions may have been made to eliminate cadmium electroplating.

I would like to suggest that cadmium electroplating can be made safe at some cost. If the cost is too high, we will accept the consequences. To eliminate cadmium plating by an apparent "gentleman's agreement" is unfair to an industry.

"Are most alternatives to electroplated cadmium available today?" Mr. Laurilliard has demonstrated that there is no universal substitute for cadmium plating, and that there is no one coating which will do the job.

Mr. Grobin has demonstrated that if you are interested in a specific characteristic, such as corrosion resistance, then zinc electroplating can do the job. Each individual application must be looked at on its merits, and looked at with a full awareness of all the different characteristics demanded by that particular application.

The effect on the quality of life could be serious if somebody were to use a poor protective coating for the landing gear of a jet plane, or for automotive applications. We must make these changes responsibly.

I do not think alternatives are available until we have (a) done correct testing, including seller's testing, and (b) until we have specifications which cover the situation adequately.

MR. ISLER: Bill Isler, Harry Diamond Laboratories. I would like to say that the quality of life should be discussed in all aspects. I think the people who got the disease which is called "Itai-Itai", are also concerned about the quality of life.

MR. GROBIN: I think it is most important to look at the reference that has been written about that, which is called "Cadmium in the Environment" put out by the Chemical Rubber Company. It clearly points out that there were other factors here. These people had a severe Vitamin D deficiency which had an impact on the uptake of the cadmium. The cadmium may not have been the culprit. There is no conclusive evidence that cadmium is the culprit. It was the first item to be pointed out. Again, the cadmium in their food chain came about by abuse and by careless operations, which is generally not the case here in the United States.

MR. SNYDER: And the water pollution came about from a mining operation rather than an electroplater. There is, of course, considerable difference.

MR. ISLER: The studies that Mr. Snyder mentioned were not universally accepted. It is like any other thing, be it smoking or whatever, I think people who are concerned about health are going to choose one side or the other.

If we cut down on cadmium, it is going to hurt the standard of living of people who work in that industry. The picture painted by this panel is that airplanes are going to fall from the skies without cadmium. This may or may not be true. Most people think that if you really need cadmium for an application, then use it. This was the result of the IBM study. They kept cadmium where they really needed it. But to argue that the whole industry has to be saved in the face of the potential health hazards is not acceptable.

MR. SNYDER: My point was that the literature produced by very reputable organizations is, in fact, quite contradictory. What I am calling for is a further study, a study which hopefully will ease out the contradictions. We platers work here, but we live here too. In fact, most of us live near our shops, and we get the impact from pollution right away close to home.

What we are asking for is to remove the contradictions in the study and define the real problem, not to wipe out a segment of an industry if we don't have to. If we do have to, fine, let's do it. But let's make sure that its necessary first. Let's bear in mind that we platers are also under rather rigid restraints with respect to water pollution. It may get more rigid over night. I refer to HR 3199. We may wind up going to such exotic pollution control systems that we are going to be at zero discharge anyway. So before we completely remove cadmium from the list of things to be used, let's consider all of this in the same mode and mood that we did here over the last few days. I am tremendously pleased to have been here. I am just really pleased that such a session was held. I will wave the flag. I think it is a fine example of how democracy is supposed to work.

MR. ISLER: The only point I wanted to make was that in setting up the workshop we tried to include view points on all aspects of the problem. This afternoon, for the last few minutes, it has been very one-sided.

MR. COOK: May I say that the gentleman seems to place himself on one side of the fence, and the panel on the other. That should not be. I don't see it that way. I see us on the same side of the fence. The heavy metals industry is saying it can operate safely. The regulatory agencies have a responsibility, and the law will be obeyed. Given that, you have safe operations for cadmium plating. We are not, therefore, talking about anything other than the economics of the situation. Of course, the environmental restrictions will affect the economics, and that is acceptable.

MR. MEYER: Fred Meyer, Air Force Materials Lab. I think you have led to some misrepresentations of the use of electroplated cadmium on landing gears. We prohibit the use of electroplated cadmium on most of the landing gears with 180,000 psi or greater strength steels. We have used vacuum deposited cadmium for the Air Force military and very probably the commercial airlines. The high strength steels are very susceptible to hydrogen embrittlement.

The major landing gear manufacturers have been using vacuum deposited cadmium for a number of years.

MR. SNYDER: The Douglas DC10 has many major components of its landing gear made from 300-M steel. The stress level is 275,000 to 305,000 psi. These parts are plated with low hydrogen embrittlement cadmium. The space shuttle utilized the same stress level, and the same material. The parts were plated with titanium cadmium. The same is true of the L-1011. The same is true with variations in material and stress levels of the 747 and 727. I know this since I plate these parts.

MS. ZILEK: I am Ms. Zilek from the Ford Motor Company. According to Mr. Menzie of the Fish and Wildlife Service, the zinc levels that were deleterious to the health of fish were far more harmful than cadmium was to fish. Is this another inconsistency, or is it true? If it is true, then why aren't we addressing zinc alternatives? If it isn't, then the environmental evidence is very weak and needs a lot more investigation before alternatives should be addressed.

MR. COOK: I think I would agree with you. We need a good deal more medical evidence. Zinc has a relatively high toxicity to marine life. However, most of us in this audience are probably zinc deficient and would probably benefit by taking zinc supplements. The point I am making is that there is a tendency to generalize from effects on fish to effects on humans. We must be absolutely sure of our facts first.

MR. GROBIN: It really doesn't make any difference whether we are talking about electroplated cadmium or vacuum deposited cadmium. Either one of those articles is going to add cadmium back into the environment. So I think we have a larger question. Is it the electroplating or metal finishing industry that is adding this cadmium to the environment and creating the "so-called cadmium hazard"? Is it the naturally occurring cadmium bearing ores that are putting the cadmium into the environment? Is it the use of cadmium pigment? Is it the use of cadmium catalysts?

We really don't know which of these items is the culprit, if there is one. The burning of coal is another one. There are many, many sources which release heavy metals into the environment. I think people have jumped to the conclusion that the electroplating industry is the culprit. I don't think the electroplating industry alone is guilty.

MR. WHITE: Actually, an EPA report does suggest that the manufacturer of nickel-cadmium batteries pollutes the environment in making the sintered plates. I haven't seen a workshop on alternatives to nickel-cadmium batteries being arranged.

MR. COOK: The International Lead Zinc Research Organization is charged with research in these areas, finding new applications of metals, lead, zinc, and cadmium. A very substantial part of our budget is related to hygiene aspects of cadmium. The industry is doing its part in this direction.

We are looking for research areas on nickel-cadmium batteries which can be helpful in reducing environmental losses. One way would be to assure the efficient recycling of the cadmium from the nickel-cadmium batteries. We at ILZRO are looking into this very seriously. Perhaps the most beneficial applications for cadmium will turn out to be those where very close control on the recycling can be achieved.

MR. DAGE: I am Elbert Dage from the Office of Toxic Substances, Environmental Protection Agency and one of the co-sponsors for this workshop. We seem to be drifting away from the topic question. I personally agree with many of the statements made here concerning the controversy over toxicity and environmental effects, and many of the other comments that were made about having industry involved earlier in this kind of discussion. In my opinion, it is very early in the game even at this point to be holding such a workshop. However, it was felt by the various agencies involved that we wanted to begin this kind of discussion, to learn more about the usage, to learn whether it is possible to clean up the electroplating industry with respect to cadmium, and to learn whether it is possible to find alternatives which might be less toxic or safer for the environment. This is the purpose of the workshop.

I think the question we are working on now is "How essential is the electrodeposited cadmium?" I am not so sure that a lengthy discussion of the debatable aspects of the health effects is appropriate here except to say that cadmium is not the only toxic metal that is used in metal finishing.

MR. SNYDER: I think we were addressing the economic effect of removing electroplated cadmium as it pertained to each of us.

MR. BOOKER: Jonathan Booker of Brush Wellman. We are talking about cadmium now as a toxic material. In substituting for cadmium, one of the considerations is that cadmium is a heavy metal. The substitutes that I have heard suggested most often are also heavy metals and also have evidence of toxicity associated with them. My overall question is whether or not this is just a beginning, or whether we should consider all of these things in the proper context as to what we need to do in order to relieve the input of toxic materials to the environment. Will we next be discussing zinc, tin, or lead in this manner? Is this just the beginning? Was this Workshop on cadmium meant to save the cadmium industry, or to take the larger issue of heavy metal pollution into consideration?

MR. GORDON: Phil Gordon, Cutler-Hammer. I think there is a language difficulty in the subject for the panel, and I would like to respond to Mr. Dage's comment.

The title is, "How essential" et cetera. You don't put those two words together. It is like saying something is "very unique". It is either essential or it is not essential. More appropriately we are looking at what are the essential uses of cadmium. The unessential uses are defined by those applications for which acceptable alternates can be found, if there is motivation to change. That way, the environmentalists, the people who support life, can make their case by saying that there are social, political, and economic benefits to limiting the use of cadmium in a specific application at the cost of this observable adequate substitute.

In applications where we have no substitute, that is a victory for the other side. Ultimately, that is what we have to find out.

MR. SNYDER: There are about four of us here who have talked about being on sides. I really hope that we are not. I hope that this is a cooperative effort, one that we are trying to put together to everybody's advantage; the environment, the industry. I, for one, will quickly say that I forego any thought of being on one team or the other. I really hope we can put this thing together and make it work. The hope that I am trying hardest to establish dovetails with

Bert Cook's. It is my personal belief that we can, if given the opportunity, establish controls so that cadmium electroplating can continue to exist.

MR. BAYNE: Mike Bayne, Battelle-Northwest. Obviously from my talk, you knew that I was very unfamiliar with what cadmium plating was until I came here this week. I have really had an education. One thing has crossed my mind. No matter what we do, the earth is always going to have "X" amount of cadmium. We are not going to destroy it, we are not going to make any more. When man starts using the natural resources, he is redistributing material. That is all he is doing, just redistributing material. If it becomes concentrated in an area and it is a bad material, it can affect the other things around it.

We can go ahead and use it, realizing that it may have some bad effects with a high concentration in a populated area. It may mean that some process has to be moved to a more isolated area. That is another alternative that has not really been discussed. Cadmium effects are worse when you bring the large volume processing into an area where you have a large population concentration. If you could move large volume processing to low population density areas, I think it would considerably alleviate the problem.

MR. SNYDER: Thank you. Hearing nothing more from the floor, I would like to take this opportunity to extend my personal thanks to all of you for your courtesy.

MR. DYCKMAN: In closing, I think something important has happened during the last three days. I think we have had a dialogue that could possibly determine the fate of a material. The purpose of sessions such as this is to bring out such issues and increase our mutual state of knowledge. This Workshop is now adjourned.

APPENDIX III

Attendance List

APPENDIX III

GOVERNMENT-INDUSTRY WORKSHOP ON ALTERNATIVES FOR CADMIUM ELECTROPLATING IN METAL FINISHING

National Bureau of Standards
Gaithersburg, Maryland

October 4-6, 1977

Registration List

Devereaux Barnes
EPA
401 M Street
Washington, DC 20460

Charles S. Bartek
RCA Corporation
Corporate Standards Engineering
Building 204-1
Camden, NJ 08027

I. Bartkey
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Don W. Baudrand
Allied-Kelite Division
Richardson Company
29111 Milford Road
New Hudson, MI 48165

M. A. Bayne
Battelle-Northwest
231-Z Building
200-W Area
Richland, WA 99352

John Bihl
Tin Research Institute
483 West Sixth Avenue
Columbus, OH 43201

John F. Binnie, Jr.
Hughes Aircraft Co.
P. O. Box 11337
Tucson, AZ 85734

Michael L. Bless
Naval Air Engineering Center
Code 9151 Bldg. 562
Lakehurst, NJ 08733

David G Blundell
Naval Underwater Systems Center
Bldg. 990 Third Floor Code 36122
Newport, RI 02840

Jonathan Booker
Brush Wellman
17876 St. Clair Avenue
Cleveland, OH 44110

John E. Breen
Ray Cheom. Company
Sudbury, MA 01776

Bob Brookshire
Brooktronics Engr. Corp.
405 Main Street
Laurel, MD 20810

Norm Camire
G & H Technology, Inc.
1649 - 17th Street
Santa Monica, CA 90404

C. R. Campbell
Monsanto Chemical Intermediates Co.
P. O. Box 12830
Pensacola, FL 32575

Douglas A. Cardwell
Goodyear Aerospace Corporation
1210 Massillon Road
Akron, OH 44315

James A. Clanton
RCA Corporation
Building 17A3-1
Camden, NJ 08102

Lester Coch
Waldes Kohinoor, Inc.
47-16 Austel Place
Long Island City, NY 11101

Frank J. Cole
Republic Steel
2906 Liggett
Parma, OH 44134

Richard J. Comp
Burndy Corporation
Richards Avenue
Norwalk, CT 06856

Walter P. Conrardy
U.S. Air Force Materials Lab.
AFML/MX
Wright Patterson AFB, OH 45433

Albert R. Cook
International Lead Zinc Research
Organization Inc.
292 Madison Avenue
New York, NY 10017

Anthony Corvelli
Naval Underwater Systems Center
Newport, RI 02840

Henry Crein
Engineering Directorate
Rock Island Arsenal
313 E. Central Pk.
Davenport, IA 52803

Elbert L. Dage
Environmental Protection Agency
Office of Toxic Substances
401 "M" Street, S.W., WH-557
Washington, DC 20460

E. A. Davis
3M Company
23923 Research Drive
Farmington, MI 48024

Wentzle R. Deboskey
IBM E81/B101
P. O. Box 12195
Research Triangle Park, NC 27709

P. Debruyn
National Bureau of Standards
Washington, DC 20234

Jon A. deRidder
Diamond Shamrock Corp.
P. O. Box 127
Chardon, OH 44024

William E. Desjardins
Reilly Plating Company
17725 Dora Avenue
Melvindale, MI 48122

J. W. Dini
Sandia Laboratories
Division 8312
P. O. Box 969
Livermore, CA 94550

A. P. Divecha
Naval Surface Weapons Ctr. (WR-32)
White Oak Lab
Silver Spring, MD 20910

Howard J. Dolejs
Gould Inc.
18901 Euclid Avenue
Cleveland, OH 44117

John G. Donaldson
ITT Cannon
666 East Dyer Road
Santa Ana, CA 92702

Fred W. Drosten
U.S. Army Aviation Research
and Development Command (AVRADCOM)
DRSAV-EQA
P. O. Box 209
St. Louis, MO 63166

Edward J. Dyckman
DOD-Defense Industrial Resources
Support Office
Cameron Station
Alexandria, VA 22314

Adolphe J. Edwards
Harry Diamond Laboratories
2800 Powder Mill Road
Adelphi, MD 20783

John Edwards
Bunner Hill Co.
P. O. Box 29
Kellogg, ID 83837

Edwin Eiswerth
Copper Range Company
Hussey Metals
310 Washington, ST.
Leetsdale, PA 15056

Anthony O. Facciolo
Alexandria Metal Finishers, Inc.
100-106 S. Early Street
Alexandria, VA 22304

E. R. Fannin
McDonnell Douglas
Box 516
St. Louis, MO 63166

James P. Flashery
Lockheed Missiles & Space Co.
121 Smith Creek Drive
Los Gatos, CA 95030

Diana B. Friedman
U.S. Dept. of Commerce-
BDC-Materials Division
Washington, DC 20230

John Fogarty
Bendix Corporation
E.C.D.
Sidney, NY 13838

Richard Funke
Allen-Bradley Company
1201 South Second Street
Milwaukee, WI 53204

R. E. Geisert
Gould Incorporated
18901 Euclid Avenue
Cleveland, OH 44117

Rein H. Gercke
Mail Stop 1/467
Aeronutronic Division
Ford Aerospace & Comm. Corp.
Ford Road
Newport Beach, CA 92663

Ralph W. Gertz
Westinghouse Plant Apparatus
Division
P. O. Box 1047
Pittsburgh, PA 15230

E. Gileadi
Institute of Chemistry
Tel Aviv University
Ramat Aviv
ISRAEL

Thomas L. Gleason, III
U.S. EPA ORD/OAWU RD682
401 M Street SW
Washington, DC 20046

Philip M. Gordon
Cutler-Hammer, Inc.
4201 N. 27th Street
Milwaukee, WI 53216

Allen W. Grobin, Jr.
IBM Corporation
P. O. Box 390
Poughkeepsie, NY 12602

Earl Groshart
The Boenig Company
20304 N. Tapps Hwy
Sumner, WA 98390

Gail M. Grove
Dow Corning Corporation
Business Research Dept.
3295 E. Wackerly Road
Midland, MI 48640

Rafael Guio
Amphenol Connector Operations
2801 South 25th
Broadview, IL 60153

William K. Halnan
Airco Temescal
2850 Seventh Street
Berkeley, CA 94710

Edward R. Hanna
Red River Army Depot
Production Engineering Division
Building 315/3
Texarkana, TX 75501

Lawrence D. Haworth
Raytheon Company
141 Spring Street
Lexington, MA 02173

Bob Heidersbach
Ocean Technology, Inc.
Box 450
Middletown, RI 02840

F. T. Henry
Lockheed-Georgia Company
Department 71-11, Zone 54
86 South Cobb Drive
Marietta, GA 30063

John Herron
Switchcraft, Inc.
5555 N. Elston Avenue
Chicago, IL 60630

Harry Hicks
Boeing Commercial Airplane Co.
Org. B-3020, M/S 64-05
P. O. Box 3707
Seattle, WA 98124

John D. Hoffman
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Philip Horelick
Allied Metal Finishing Corporation
4000-4008 E. Monument Street
Baltimore, MD 21205

E. Horowitz
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Ralph J. Hovey
Amphenol
2801 S. 25th Avenue
Broadview, IL 60153

William Hratko
Sundstrand Aviation
4747 Harrison Avenue
Rockford, IL 61101

William E. Isler
Harry Diamond Laboratories
2800 Powder Mill Road
Adelphi, MD 20783

Edward Jankowsky
Naval Air Development Center
Code 30221
Warminster, PA 18974

Martin A. Jaros
Rockford Products Corporation
707 Harrison Avenue
Rockford, IL 61101

James V. Jeffreys
Defense Construction Supply Center/SE
3990 E. Broad Street
Columbus, OH 43215

Ronald B. Johnson
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Jack L. Johnston
Naval Mine Engineering Facility
(NAVMINENGRFAC)
Test Engineering Department
Yorktown, VA 23691

Edward Jorczyk
3M Company
Plating Systems Department
Building 53-1
367 Grove Street
St. Paul, MN 55101

Sam Kann
TRW/Cinch
1500 Morse Avenue
Elk Grove, IL 60007

William B. Kerfoot
Environmental Devices Corporation
Tower Building
Marion, MA 02738

Ed Killian
Waldes Kohinoor, Inc.
47-16 Austel Place
Long Island City, NY 11101

John R. Kovelan
Diamond Shamrock
Metal Coatings Division
P.O. Box 127
Chardon, OH 44132

Theodore J. Kozan
Boeing Wichita Company
Material and Processes Engineer
3801 South Oliver
Wichita, KA 67210

Gerald G. Kraft
Kraft Chemical Company
917 West 18th Street
Chicago, IL 60608

Paul A. Krasley
Bureau of Engraving and Printing
14th and C Streets, SW
Washington, DC 20228

David R. Kverek
Martin-Marietta Aerospace
MP 194
P. O. Box 5837
Orlando, FL 32805

W. W. Ladyman
Vought Corporation
P. O. Box 5907
Dallas, TX 75222

Robert W. Lancaster
Bradford National Corporation
2 Research Place
Rockville, MD 20850

Paul Lancer
Consumer Product Safety Commission
5401 Westbard Avenue
Room 732
Bethesda, MD 20207

John Lavrilliard
Standard Pressed Steel Company
Highland Avenue & Mt. Carmel Ave.
Jenkintown, PA 19046

F. W. Lawrence
Empigard Corp.
2820 E. 90th Street
Cleveland, OH 44104

Mark Lazarz
Cutler-Hammer Inc.
4201 N. 27th Street
Milwaukee, WI 53216

G. M. Legard
Bunker Hill Co.
P. O. Box 29
Kellogg, ID 83837

Patrick Leonard
Army Materials & Mechanical
Research Center
Watertown, MA 02172

C. Levy
U.S. AMMRC
Arsenal Street, Bldg. 312
Watertown, MA 02172

Donald V. Levy
Lockheed Research 5235/204
3251 Hanover
Palo Alto, CA 94304

Jack B. Levy
General Electric Company
120 Erie Blvd.
Schenectady, NY 12305

Elmer A. Lord
Harshaw Chemical Company
1945 East 97th Street
Cleveland, OH 44106

John M. Lucas
U.S. Bureau of Mines
2401 E. Street NW
Washington, DC 20241

Donald Lyman
International Lead Zinc
Research Organization
292 Madison Avenue
New York, NY 10017

Albert Lyon
Fag Bearing Corporation
42 Bennett Street
Stamford, CT 06907

Joseph W. Macedo
Martin Marietta Corporation
4613 Longworth Drive
Orlando, FL 32806

Robert F. Martin
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

James M. Mayer
3M Company
3M Center 223-4NE
St. Paul, MN 55119

L. McClendon
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Kenneth E. McCullough
Standard Pressed Steel Co.
Jenkintown, PA 19046

Mattie F. McFadden
Raytheon Company
Hartwell Road
Bedford, MA 01730

Fred H. Meyer, Jr.
Air Force Materials Lab
Wright Patterson AFB, OH 45433

Guy F. Morris
Northkop Corporation
Aircraft Division
3901 West Broadway
Hawthorne, CA 90250

Donald E. Muehlberger
McDonnell Douglas Corporation
P. O. Box 516
St. Louis, MO 63166

R. A. Munson
Bureau of Mines
2401 E. Street NW
Washington, DC 20241

E. E. Oberland
Chesapeake Metal Finishing Corporation
4010 North Point Blvd.
Baltimore, MD 21222

F. Ogburn
National Bureau of Standards
Washington, DC 20234

William L. Pagels
Grumman Aerospace Corporation
Bethpage, NY 11714

Marlin D. Peace
Red River Army Depot
Production Engineering Division
Building 315/3
Texarkana, TX 75501

Edward A. Peak
Fitzgerald Plating Co.
17450 Filer
Detroit, MI 48154

Walter Petro
Ideal Corporation
1000 Pennsylvania Avenue
Brooklyn, NY 11207

Theodore M. Pochily
U.S. Department of Army
Watervliet Arsenal
736 Pearse Road
Schenectady, NY 12309

Kee J. Pon
Naval Ship Engineering Center
Code 6101D
Washington, DC 20362

Richard Pope
The Weatherhead Company
300 East 131 Street
Cleveland, OH 44108

Edward H. Poplawski
Sperry Gyro Company
Union Turnpike
Great Neck, NY 11020

William H. Quittman
Defense Industrial Supply Center
DISC-ECM
700 Robbins Avenue
Philadelphia, PA 19111

A. J. Raffalovich
U.S. Army Electronics Command
DRSEL-TL-ME
Fort Monmouth, NJ 07703

C. Reimann
Institute for Materials Research
National Bureau of Standards
Washington, DC 20234

Dell L. Replogle
Reytheon Co.
  Electromagnetic Sys. Div.
6380 Hollister Ave.
P. O. Box 1542
Goleta, CA 93017

George A. Risko
Chrysler Corp.
  Sterling Defense Division
6000 East 17 Mile Road
Sterline Heights, MI 48078

Narvel L. Rogers
Bell Helicopter Textron
P. O. Box 482
Fort Worth, TX 76101

Donald J. Sargent
E/M Lubricants, Inc.
P. O. Box 2200
W. Lafayette, IN 47906

Bruce D. Sartwell
U.S. Bureau of Mines
College Park Metallurgy Res. Ctr.
College Park, MD 20740

J. W. Sarvis
Department of Defense
D.M.S.S.O.
Cameron Station
Alexandria, VA 22314

Robert Scannell
McDonnell Douglas
2600 N. 3rd
St. Charles, MO 63301

S. R. Schachameyer
Cutler-Hammer, Inc.
4201 N. 27th Street
Milwaukee, WI 53216

James E. Schell
Alumatec Corporation
332 No. "A" Street
Lompoc, CA 93436

A. J. Schwarz
Gould Inc.
Valve & Fittings Division
6300 West Howard Street
Chicago, IL 60648

Daniel Seymour, Jr.
Physical Sciences Laboratory
  Sacramento Air Logistics Command
McClellan Air Force Base
Sacramento, CA 95652

Gene Simmons
Sermetel Inc.
155 South Limerick Road
Limerick, PA 19468

James R. Simmons
MS 3516
Martin Marietta Aerospace
P. O. Box 29304
New Orleans, LA 70189

Bonnie Simpers
Grumman Aerospace Corporation
Plant 12, Dept. 447
Bethpage, NY 11714

John H. Sizer, Jr.
Pratt & Whitney Aircraft
Mail Stop MERLJ Bldg.
400 Main Street
East Hartford, CT 06066

Samuel Sizgorich
Defense Industrial Supply Center
(DISC-E)
700 Robbins Avenue
Philadelphia, PA 19111

R. P. Skow
B. F. Goodrich
Engineered Systems Division
Box 340
Troy, OH 45373

W. E. Snyder
MFASC
236 Pageantry Drive
Placentia, CA

Jerry Stockdale
Naval Avionics Facility
1510 N. Leland
Indianapolis, IN

Harry Stollberg
Allen-Bradley Company
1201 South Second Street
Milwaukee, WI 53204

Richard Sussman
AVCO, Lycoming Division
550 S. Main Street
Stratford, CT 06497

Edward Taylor
Standard Pressed Steel Company
Highland Avenue
Jenkintown, PA 19046

Don Teter
Techno-Economic Services Co.
8343 Hammerly Blvd.
Houston, TX 77055

J. N. Tuttle, Jr.
Rust Proofing & Metal Finishing Corp.
55 Commercial Street
Medford, MA 02155

Luther Vaaler
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Ed J. Violante
Ford Motor Company
Am Road
Dearborn, MI 48126

James E. Voytko
Western Electric Co. Inc.
2000 NE Expressway
Atlanta, GA 30071

George Waldes
Waldes Kohinoor, Inc.
47-16 Austel Place
Long Island City, NY 11101

Sheldon Wesson
American Metal Market
665 National Press Building
Washington, DC 20045

Leslie Westerling
B. F. Goodrich Company
Box 340
Troy, OH 45373

Martin S. White
Cadmium Association
34 Berkeley Square
London, UK

Vernon H. Wilson
3M Company
Plating Systems Department
3M Center, Bldg. 223-4M.E.
St. Paul, MN 55101

Alan Winchell
General Electric Company
Box 5000 MD070
Binghamton, NY 13902

LuVern J. Wooge
Naval Ordnance Station
Indian Head
Indian Head, MD 20640

Jack Yost
Purdue University
West Lafayette, IN 47906

Joseph A. Zehnder
Enthone Inc.
P. O. Box 1900
New Haven, CT 06508

Hank Zielinski
Federal Screw Works
3401 Martin
Detroit, MI 48210

Carolyn Zilek
Ford Motor
Bldg 5 Room 1008
Dan Mich
Dearborn, MI 48121

APPENDIX IV

Sponsoring Agencies and Representatives

APPENDIX IV

MEMBERS OF THE INTERAGENCY STEERING COMMITTEE RESPONSIBLE FOR PLANNING THE GOVERNMENT-INDUSTRY WORKSHOP ON ALTERNATIVES FOR CADMIUM IN METAL FINISHING

Mr. Dev Barnes
Effluent Guidelines Division
Office of Water Planning & Standards
WH-552
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Phone 426-2586

Mr. Allen Cywin
Senior Science Advisor
OWHM (WH-556)
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Phone: 755-0330

Mr. Elbert Dage *
Hazard Assessment Group
Office of Toxic Substances
WH-557
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Phone: 755-2110

Mr. Edward Dyckman **
Defense Industrial Resources
Support Office
Cameron Station
Alexandria, VA 22314
Phone: 274-7222

Mr. John Flack
Standards & Quality Control
Federal Supply Service
General Services Administration
Washington, D.C. 20406
Phone: 557-8660 or 7537

Mr. John Hague
U.S. Bureau of Mines
2401 E Street, N.W.
Washington, D.C. 20241
Phone: 634-1063

Mr. Ernst Hall
Effluent Guidelines Division
Office of Water Planning & Standards
WH-552
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Phone: 426-2576

Mr. William Isler
Bldg. 204, 4C-104
Harry Diamond Labs
2800 Powder Mill Road
Adelphi, MD 20783
Phone: 394-3190

Mr. Paul Lancer
Bureau of Engineering Sciences
Consumer Product Safety Commission
Room 900
5401 Westbard Avenue
Bethesda, MD 20207

Mr. Pope Lawrence
Office of Federal Activities
(A-104)
Environmental Protection Agency
Washington, D.C. 20460
Phone: 245-3006

Dr. Joseph McLaughlin
Bureau of Biomedical Science
Consumer Product Safety Commission
5401 Westbard Avenue
Bethesda, MD 20207
Phone: 492-6480

Mr. Calvin Menzie
Division of Habitat Preservation
Research
Fish and Wildlife Service
Department of the Interior
Washington, D.C. 20240
Phone: 343-4670

** Chairman*

*** Coordinator*

Mr. Fielding Ogburn
Metallurgy Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234
Phone: 921-2957

Mr. Wade Talbot
Office of Health & Ecological
Effects/ORD
RD-683
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460
Phone: 755-9722

Mr. Grover Wrenn, Director
Division of Health Standards
Occupational Safety and Health
Administration
Department of Labor
200 Constitution Avenue
Washington, D.C. 20210
Phone: 523-7177

APPENDIX V

Aerospace Industries Association

Surveys on Alternatives to Cadmium Plating

Preceding page blank

AEROSPACE INDUSTRIES ASSOCIATION OF AMERICA, INC.
1725 DE SALES STREET, N.W., WASHINGTON, D.C. 20036 TEL. 347-2315

December 20, 1977

Mr. Edward J. Dyckman
Defense Industrial Resources Support Office
Department of Defense
Dwyer Building
Cameron Station
Alexandria, Virginia 22314

Subject: AIA Surveys on Alternatives to Cadmium Plating

Reference: Government/Industry Workshop - October 4=6, 1977

Enclosure: (A) Summary and Comments to AIA Survey on Cadmium Plating Replacement

(B) Summary of Comments to AIA Survey on Role of Specifications and Standards on Adoption of Alternatives for Cadmium Electroplating in Metal Finishing

Dear Mr. Dyckman:

The enclosures are two AIA surveys conducted on alternatives for cadmium electroplating.

The survey of Enclosure (A) was conducted by the National Aerospace Standards Committee with the objective of determining feasible alternatives should restrictions be placed on the use of cadmium plating.

Enclosure (B) contains the results of a survey conducted by the Materials and Structures Committee to provide comments for the workshop panel discussion: "Are Specifications and Standards Barriers to Change?"

You are free to use this material in your Workshop Proceedings if you so desire.

Very truly yours,

AEROSPACE TECHNICAL COUNCIL

J. P. Reese, Executive Secretary
Materials and Structures Committee

JPR/sfe
cc: M. McFadden

SUMMARY AND COMMENTS TO AEROSPACE INDUSTRIES ASSOCIATION SURVEY QUESTIONNAIRE ON CADMIUM PLATING REPLACEMENT

Twenty (20) users and seven (7) suppliers responded to the survey

1. If E.P.A. requirements eliminate the use of cadmium plating, what alternate fastener finish would you use of general application when installed in the following structure.

1.1 Aluminum Sheet

1.1.1 Aluminum, IVD Coating

(7) Users
(2) Suppliers

1.1.2 Aluminum Coating

(7) Users
(1) Supplier

1.1.3 Zinc (Plate or IVD)

(4) Users

1.1.4 Polysulfide Sealant

(1) User

1.1.5 Fused Tin or Solderplate

(1) User

1.1.6 Wet Sealant

(1) User

1.1.7 Primer

(1) User

1.1.8 Nickel or Chrome

(1) User

1.1.9 A286 or Chrome Fastener

(3) Users
(1) Supplier

1,2 Titanium

1.2.1 Aluminum IVD Coating

(4) Users
(2) Suppliers

1.2.2 Aluminum Coating

(4) Users
(1) Supplier

1.2.3 Tin

(2) Users

1.2.4 Polysulphide Sealant

(1) User
(1) Supplier

1.2.5 Nickel or Chrome

(1) User

1.2.6 Dry Film Lube

(1) User

1.2.7 A286 or Cres Fasteners

(5) Users
(1) Supplier

1.3 Low Carbon Steel

1.3.1 Zine

(7) Users
(2) Suppliers

1.3.2 Aluminum IVD

(6) Users
(1) Supplier

1.3.3 Aluminum Coating

(6) Users
(1) Supplier

1.3.4 Nickel or Chrome

(2) Users

1.3.5 Polysulphide Sealant

  (1) User

1.3.6 Fused Tin or Solder

  (1) User

1.3.7 A286 or Cres Fastener

  (2) Users
  (1) Supplier

1.4 Alloy Steel

1.4.1 Aluminum IVD

  (7) Users
  (1) Supplier

1.4.2 Aluminum Coating

  (5) Users
  (2) Suppliers

1.4.3 Zinc

  (6) Users
  (2) Suppliers

1.4.4 Polysulfide Sealant

  (1) User

1.4.5 Nickel or Chrome

  (1) User

1.4.6 Fused Tin or Solderplate

  (1) User

1.4.7 A285 or Cres Fasteners

  (3) Users
  (1) Supplier

1.5 Composite Material

1.5.1 Titanium

  (6) Users

1.5.2 Aluminum IVD

(4) Users

1.5.3 Polysulfide Sealant

(1) User

1.5.4 Fused Tin or Solderplate

(1) User

1.5.5 Aluminum Coating

(1) User

1.5.6 Nickel or Chrome

(1) User

1.5.7 Zinc

(1) User

1.5.8 A286 or Crew Fasteners

(5) Users
(1) Supplier

2. Do you expect to develop such substitute capability in the future, and if so, what date?

Yes: (7) Users, (4) Suppliers

Available Now:	(3) Users, (1) Supplier
1978:	(1) User
1980:	(1) User
Unknown:	(2) Users, (6) Suppliers

No: (10) Users, (3) Suppliers

3. Do you expect any significant availability or cost problems to be associated with these substitute finishes?

No: (4) Users, (1) Supplier
Slight: (6) Users, (1) Supplier
Some possible usage, acceptance or method problems: (5) Users

Attachment (B)

AEROSPACE INDUSTRIES ASSOCIATION

SUMMARY OF COMMENTS

Survey on Role of Specifications and Standards on Adoption of Alternatives For Cadmium Electroplating in Metal Finishing

(1) Are specifications and standards barriers to change?

(A) Yes they are - especially when working on military contracts. In order to institute a change an excessive period of time is required along with considerable test documentation and even then the outcome is uncertain.

(B) Yes. Procedural specifications and standards tend to act as temporary road blocks which are slow and costly to move.

The widely used specifications require excessive coordination times and because they are specified for almost every contract, tend to have the key requirements diluted to the point of ineffectiveness.

(C) No. Requalification of alternate materials, methods and coatings to meet specifications will be required. The requirements will be the same as or very near those for cadmium plating. Rewriting will be required, but there should be no barrier to change, except for time and cost.

(D) No, these are not barriers to change. The greatest barrier is substantiation of changes by performance testing.

(F) Yes. Since specifications and standards require investment in Plant Facilities, the capitalization or amortization of facilities is a barrier.

(G) Yes. Any new thinking is resisted by Government personnel unless long, costly programs with the accompanying data are available. Even then, (Government) personnel would rather sit on what they have (provided no problems exist) than make a change based on costs or ease to the manufacturer.

(H) To a degree. Specifications and standards are invoked contractually and require contractual deviations to use something else, and deviations are usually avoided.

(J) Yes. Once hundreds of drawings call out a specification, it is costly to change.

(K) Yes.

(L) Yes, a careful check will have to be made to determine the effect of the change on the standard or specification and the associated contractual obligations involved.

(M) Yes, when they specify electroplated Cad as the required finish. e.g. standard attaching parts.

Question (1) cont'd.

(N) No, if we see more performance type specifications and fewer recipe types.

(O) Yes, since contractual requirements specifically call out cadmium plating to a Federal Specification, prime contractors specifications, and other related specifications such as AMS 2400 or AMS 2401.

(P) Specifications and standards must be barriers to undesired and/or uncontrolled changes, otherwise they would not be doing their job. Sometimes desired changes are delayed more than we would like, but the delay may be necessary and valuable in uncovering unexpected complications during the change substantiation effort.

(Q) Yes, when a process or material reaches the point in development where it is possible to describe it's requirements in a specification, and this is done, there is a tendancy to no longer pursue better ways or materials to do the job, rather, just to use the proved method or material. With time and experience these proved processes and materials become entrenched. The only motivation for any further improvements is usually brought about by a problem.

(R) Since aerospace procurement is largely controlled by specification and standards requirements, they will be barriers to change.

(2) What role will specifications and standards play in the adoption of materials and processes that are identified as viable alternatives to cadmium electroplating in metal finishing?

(A) They will have to be incorporated in MIL and FED standards dealing with protective coatings - as acceptable alternates.

(B) When specs and standards identify performance requirements instead of what has to be used, how thick and how it must be applied, then viable, cost effective alternates can and will be selected and used by the aerospace industry.

The priorities and sequence should be: (a) Identification of viable alternates (this workshop); (b) Thorough performance testing - laboratory and field; (c) Selected service applications (government approved contractor specifications); and (d) Industry, then government specifications.

(C) Standards and specifications will be required to use alternatives to cadmium plating.

(D) Specifications and standards establish the fundamental basis for utilization of alternatives.

(F) Since substitution of mechanical or vapor deposition may not fulfill the application spectrum of electroplate, additional substitutes (Zinc-rich coatings, etc) would probably result in a multiplicity of specifications and standards for alternates.

Question (2) cont'd.

(G) A major role. Specifications or standards of materials will relieve all users the necessity of writing individual requests for changes, with the required back-up data to justify the change, to the new protective systems.

(H) If specifications and standards are created, and recognized (in MIL Bulletin 400, MIL-E-5400, etc). they are more apt to be utilized.

(J) If customers require the use of new coatings, these new materials will be adopted.

(K) Essential.

(L) A very active role. It is anticipated that there is no one alternative system which can be invoked to replace our present cadmium plating.

(M) Specifications and standards will be necessary to insure uniform quality of approved alternatives to cadmium electroplating and to aid in proper use of the alternative coatings.

(N) Unless specifications and standards are initiated by some organization, changes will be long in coming.

(O) The existing viable alternatives specifications and standards will control what process or processes will be used as a substitute for cadmium.

(P) They will provide a needed common approach, shared by many aerospace users, for earlier attainment of uniformity of quality, thickness control and test methodology.

(Q) The existing requirements as described in the existing specifications and standards would continue to be the governing standard for any viable alternative to cadmium electroplating. The alternative must be equal to or better than the existing requirements.

(R) Affected specifications and standards will require "tailoring" to include and permit use of viable alternatives to cadmium electroplating as identified following demonstration of feasibility.

(3) What means should be adopted for the selection of materials, methods, and coatings for exploration as candidates for use in lieu of electrodeposited cadmium?

(A) (1) Costs; (2) Ease of application - (minimize complicated equipment); (3) Comparative corrosion tests with cadmium; (4) Types of surface

Question (3) cont'd.

(B) Government sponsored competitive research, incentive type research allowances in system hardware contracts for technological improvements in environmental protection alternates for electrodeposited cadmium.

An industry-wide survey could provide data for a parametric analysis of cadmium electroplating utilization and assist in establishment of guidelines for acceptability of alternates.

Candidate alternative characteristics to be determined include:

(a) Coating performance: Corrosion resistance, paint adhesion, wear resistance, and base for solid film lubricants.

(b) Coating properties: Porosity, galvanic potential and hardness.

(c) Effects of coating: Hydrogen embrittlement, liquid metal embrittlement, stress corrosion and galvanic coupling.

(d) Process control: configuration limits, thickness controls and appearance.

(C) All applications must be identified and analyzed to determine why cadmium was chosen for each of the applications. Based on this information, alternate materials or simple redesign will eliminate many uses of cadmium. Intelligent choices of alternates cannot be made until this survey is completed and analyzed.

(D) Proposed alternatives must be tested and proven equivalent without restriction so that each particular application does not have to be requalified.

(F) Cost, technical and environmental complexities indicate that separate programs be implemented for industrial applications and for military applications.

(G) Suggest that a six-month notice be given to coating manufacturers to provide alternative recommendations with data, to a select committee. The committee to select materials for evaluation based on the area of use, i.e., aircraft, ground support, electronics, small or major user shop. An evaluation program be written and provided to a select group of users (with Government funds) the responsibility of testing and providing the data for the select committee to evaluate alternative materials. The select committee to subsequently write the required specification (performance) and standards for the alternative materials.

(H) RFQ's for study contracts should be issued to applicable industry sources.

Question (3) cont'd.

(J) Industry groups such as AIAA or SAE should select candidate materials and gather data on real-time performance. Study should examine problem at two levels; routine corrosion protection (non-structural parts) and critical corrosion protection (structural parts such as high strength fasteners).

(K) Environmental exposure and corrosion tests are primary factors. Mechanical properties, coating cycle time and equipment cost also have to be considered.

(L) A complete outline of all the available possible changes to coatings/platings will have to be set up outlining the differences, with a comparison of properties and costs to present cadmium plate. Extensive testing may be involved to determine the effect of changes.

(M) (1) Compile candidate materials from all available sources; (2) reduce the list to a limited number of viable candidates by survey, society correspondence, etc.; (3) survey government contractors for applications where none of these candidates will work; (4) analyze problem areas individually.

(N) Action by the EPA in connection with some government subsidies would force the changes. However, off-the-shelf processes are available now without additional research.

(O) Processes that parallel electrodeposited cadmium, i.e., electrodeposited zinc should be compared against cadmium by salt fog testing, thickness-for-thickness. These two specifications, QQ-P-416 and QQ-Z-325, are more closely similar that any other processes available as substitutes.

(P) A tentative list should be submitted to AIA/MSC for ballot selection of the candidates of greatest interest.

(Q) Means - as money. Research money to replace cadmium electroplating might be hard to justify in that everything is already geared up to use it. This is particularly true of in-house funds where the only justification for change would be of necessity to meet a new requirement for pollution control or something of that nature.

Means - as testing procedures. Cadmium electroplating is primarily used in controlling corrosion. In order to evaluate alternatives, the tests would be various environmental exposure tests such as salt (fog) spray, high humidity, and outside exposure conducted using test pieces and actual parts. Cadmium, by nature, offers a coating which has an established performance to resist fretting, galling and subsequent fatigue failure. Any replacement for cadmium should be evaluated for this property, e.g. fasteners, slip fit bushings, etc. Other applications for cadmium is in lubrication. In this case, some sort of wear testing would be required.

Question (3) cont'd.

(R) A listing of promising candidate materials, methods and coatings should be jointly prepared -- designate an organization (company, lab, etc.) having the necessary capabilities and expertise to conduct the required development, evaluations and testing to prove feasibility of alternatives. The appropriate government agency should provide financial support and monitor/approve the effort and results.

(4) Many Government and technical society specifications and standards call for the use of electrodeposited cadmium as a corrosion protective coating for hardware. What would be the time, cost and procedures involved in adopting alternative materials, methods and coatings to replace electrodeposited cadmium in these and related documents?

(A) This could be very time consuming.

(B) Time - 3 to 5 years. Cost - dependent on number of candidates. Major cost impact which needs to be evaluated separately for each application:

(a) Fasteners: Coating thickness, effect on torque values, hydrogen embrittlement, fatigue, temperature limitations, galvanic and crevice corrosion and cost.

(b) Primary Structure: Hydrogen embrittlement, paint adhesion, corrosion resistance, environmental resistance, galvanic coupling and raparability.

Procedure: Test, evaluate and compare in programs as recommended in (2) and (3) above. Viable alternates will probably include zinc, tin, aluminum, alloy coatings and dry film lubricants with selection depending on substrate and use.

(C) It will require a long time to change the standards and specifications because new application criteria must be developed prior to changing to alternate materials, methods and coatings. It is visualized that extensive changes will necessitate reissuing new specifications and standards.

(D) Specific costs would be dependent upon each application and would vary also with facilities involved as well as whatever may be determined as the alternative process.

(F) We do not have the technological expertise or cost data to formulate a qualified answer to this question.

(G) If a concerted effort is made, under a schedule mandated and funded by Government, possibly two - three years at a cost of $1,500.000

Question (4) cont'd.

(H) The time and cost would be significant. Many company standards throughout industry would also require changes. Cancellation of QQ-P-416 would probably be necessary to assure full compliance. An edict prohibiting electrodeposited cadmium might also be necessary.

(J) Time, cost and procedures would depend on the alternate protective coating selected and the intended application. We have already selected aluminum coatings to replace cadmium. If alternate materials are found, new specifications should be written and imposed on new programs only.

(K) See (3). Minimum lead time of two years after acceptable alternates have been developed to incorporate in normal manufacturing operations.

(L) Our estimates are four to five years with overall costs running into the millions of dollars.

(M) Time and cost would be large for an immediate change. However, blanket substitution procedures could save both time and cost.

(N) Unable to answer.

(O) The processing equipment might involve the greatest cost and time consideration in replacing cadmium if impact deposition were used. The least replacement cost in time and procedures would be the use of electrodeposited zinc. This would merely involve replacing the electrolyte.

(P) For a completely new coating on critically stressed parts, would estimate a minimum of three years of laboratory, rig and full-scale product testing, including adjustments in the initially developed coating, followed by two to three years of field testing under normal and severe conditions. Thus, well over five year could elapse prior to production use, following initial development. Cost would depend on circumstances, but could be several million dollars for some applications. Most practical solution is to retain the ability to use cad plate, utilizing whatever means necessary to protect the environment.

Obviously there will be no single alternative which can be applied across the board. New designs can, and in some instances already do, utilize suitable replacements selected according to the specific needs, and there may be little or no cost penalty in so doing.

There is, however, no way to change all existing service applications without the possibility of adversely affecting critical parts properties and, perhaps, some other aspect of our environment. The evaluation of substitutes in all such applications would be a technical and economic nightmare.

Question (4) cont'd.

(Q) This would be an involved testing program over a fairly extensive period of time in order to assure that the replacement was reliable. As the testing program progressed, other applications or properties of cadmium that were not outlined at the outset but were of equal importance, will come to light and need to be evaluated. It is believed that there is not a universal substitute for cadmium and each property and application may require a different substitute material.

(R) A coordinated, controlled evaluation effort as described in #3 above would prevent duplications in establishing viable alternatives and would minimize costs involved. Anticipate at least a year will be required to determine and verify alternatives, and "tailor" related documents necessary to implement on a production basis.

(5) Does the use of materials vis-a-vis performance specifications influence the time and cost involved in changing over from electrodeposited cadmium to potential alternative materials, methods, or coatings?

(A) Yes.

(B) The establishment of performance specifications to define the requirements are less costly and permit the use of the most cost effective protective coating from the specific conditions the hardware will see.

(C) Yes, dependent on the alternative. Particular attention must be given to compatibility from the corrosion standpoint. We have to guarantee that the new coating will meet the same requirements as cadmium for the specific application. This will necessitate a costly requalification program in many cases.

(D) Yes, it is highly dependent on what are the alternative materials, methods or coatings.

(F) Materials - Process type specifications cannot be reliably qualified without verification by performance data.

(G) Yes, the cost of time, labor and materials required to meet qualification requirements of performance specifications always is a concern.

(H) In some cases, additional costs would be necessary for conducting environmental testing of parts to assure meeting contractual performance with an alternative coating.

(J) No - drawings still have to be changed and new processing equipment installed. A material specification is preferred because it allows better control of the product. Performance tests, such as soft-spray resistance, should be included in the specification.

A performance specification that calls for an unidentified coating that survives a specific time in a specified test atmosphere, such as on a beach exposure rack, is unacceptable.

Question (5) cont'd.

(K) Yes.

(L) Yes.

(M) Yes - performance specs are not suitable for application when it is necessary to know what coating is used. For example, contact between cadmium and titanium is prohibited, zinc is prohibited where good electrical conductivity is required, etc. Materials Specification must be available for drawing callout in order to assure that parts from all suppliers are interchangeable.

(N) Performance specifications should shorten the transition period in any change over.

(O) Yes. The influence of performance specifications will have a direct effect in change over from electrodeposited cadmium to other potential alternative materials, methods or coating. Again the alternative material and method that more closely parallels electrodeposited cadmium will have the greatest potential for change over.

(P) Performance specifications may well be the least expensive approach for eventual requirements and controls, but the potentially high cost and time for developing, proving and changing over to each new protective system will be the same either way.

(Q) Yes, but some performance specification is necessary to be able to compare the alternative material with the cadmium plate. However, if the alternative material is one where experience and testing has shown that it is equivalent, a performance specification may not be required and therefore would be less expensive with regard to time and cost.

(R) Yes - Other factors involved are pollution control/waste disposal requirements and costs associated with alternatives developed. Are they more or less stringent or about the same as that required for the electrodeposited cadmium coating process.

APPENDIX VI

Results of Workshop Questionnaires

Preceding page blank

RESULTS OF QUESTIONAIRE
DISTRIBUTED TO PARTICIPANTS AT THE WORKSHOP
ON
ALTERNATIVES FOR CADMIUM ELECTROPLATING IN METAL FINISHING

Thirty-nine out of 160 or 24% of the Workshop attendees responded to a feedback questionnaire distributed at the Workshop on Alternatives for Cadmium Electroplating in Metal Finishing. A summary of the response to the questionnaire follows. Since a number of respondees gave more than one answer per question, the responses are categorized in percentages.

QUESTION 1 - "Why have you attended this Workshop?"

RESPONSE	% OF RESPONSE
To learn of alternative materials and processes.	47
To learn of the future of electrodeposited cadmium.	21
To keep up with the state-of-the-art in metal finishing.	12
To represent the interest of cadmium platers.	10
To learn of issues related to the use of specifications and standards and the adoption of new materials and processes.	6
To learn of government and industry activities regarding toxic substances.	4
	100

QUESTION 2 - "Are you satisfied with the Workshop?"

RESPONSE	% OF RESPONSE
Yes	87
Somewhat	10
No	3
	100

QUESTION 2 - "Explain Why or Why Not?"

RESPONSE

Positive: Most were impressed with the organization, punctuality, balance of views, and comprehensiveness of the conference.

Negative: Didn't care for panel sessions.
Didn't care for some industry papers because they were self-serving and not technical.

RESPONSE

Negative: (Cont.)
Didn't adequately address alternatives for cadmium electroplating on electrical and electronic hardware.
Would like to see proceedings issued sooner.

RECOMMENDATIONS:

Should have included both industry and NATO representatives on the Steering Committee.
Should have been held even earlier in the process of government deliberations on cadmium.
Suggest problems of hazards to the environment be addressed to the entire plating industry in the form of a workshop.

QUESTION 4 - "Unanswered Questions".

What alternatives are there for cadmium electroplating on non-ferrous substrates in electrical applications? (Philip Gordon, Cutler-Hammer, Inc.).
What would best solve the problem of cadmium pollution - mandatory controls by government or voluntary industry adoption of alternatives to cadmium electroplating? (William Hratko, Sundstrand Aviation).
Has a decision been made by government that effluent guideline controls will not be effective for cadmium pollution and, therefore, some other regulatory actions needs to be promulgated? (Albert Cook, International Lead Zinc Research Organization, Inc.).
What are some effective methods of attaining zero discharge of cadmium in plating shop effluents other than by a closed loop system? (Seymour Daniel).
When will restrictions in the use of cadmium be issued by EPA? (Edward Hanna, Red River Army Depot).
Once these restrictions are announced, how much lead time will be given to convert to alternative coatings? (E. Hanna).
Once these restrictions are announced, what alternative coatings will DoD adopt? (E. Hanna).
How should cadmium plated articles be disposed of once their useful life is over? (LuVern Wooge, Naval Ordnance Station).
What are the views of EPA regarding future restrictions to be placed on the cadmium plating industry? (Edward Taylor, Standard Pressed Steel Company).
How will evaluation, qualification, and use of alternatives for electrodeposited cadmium by DoD contractors be funded? (Mattie McFadden, Raytheon Company).
Where will facilities for these alternative processes be installed - in DoD contractor plants or independent job shops? (M. McFadden).

QUESTION 4 - "Unanswered Questions". (Cont.)

Is there any attempt being made to standardize military finish standards (e.g., MIL-STD - 171, 186, 193, 194 and MIL - F - 14072)? (George Risko, Chrysler Corporation).

What are the exact steps one takes to develop new specifications and standards? What is the source of funding of this work? This is in reference to the adoption of alternative materials and processes for electrodeposited cadmium. (Michael Bayne, Battelle - Northwest).

Will there be any recommendations generated as a result of this meeting? (Edward Jankowsky, Naval Air Development Center).